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π-Bond Dissociation Energies: C−C, C−N, and C−O

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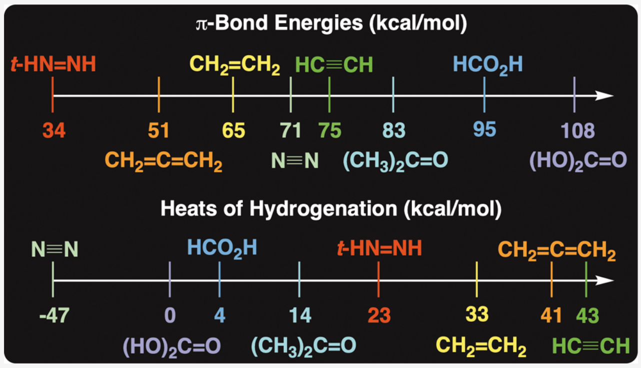
ABSTRACT: Single, double, and triple bond dissociation energies are useful quantities, but students and practicing chemists commonly do not know representative values or how they are obtained. In this paper, select π-bond energies are provided and general methods for their determination are discussed. Relationships between heats of hydrogenation, bond dissociation energies, and π-bond strengths are also addressed.



■ INTRODUCTION

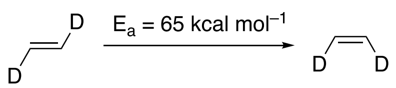
Bond dissociation energies (BDEs) for σ-bonds are well-defined quantities corresponding to the enthalpy for their homolytic cleavage (i.e., eq 1, where X and Y represent any atom or group of interest). A variety of different experimental approaches have been developed for measuring these quantities and given their utility and fundamental importance, they have been widely reviewed and are commonly provided in chemistry textbooks, journal articles, and book chapters.[1−10]

$$\text{X−Y} \rightarrow \text{X}^\bullet + \text{Y}^\bullet \;\; \Delta H^\circ_{\text{rxn}} = \text{BDE(X−Y)} \tag{1}$$

The bond strength of a π-bond (E_π) cannot be directly measured since molecular fragments are not formed upon its cleavage and the resulting noninteracting singlet biradical is only a conceptual construct, not an observable species on the potential energy surface. Nevertheless, students are taught early on that π-bonds are weaker than σ-bonds and 65 kcal mol^{-1} is a typical carbon−carbon π-bond strength. Selected E_π values are also provided in some textbooks,[9,10] but students and practicing chemists alike often do not know how these quantities are determined and are unfamiliar with other representative values. In this discussion I explain how E_π is obtained and give selected results using energetics from the Active Thermochemical Tables (ATcT) database[11] as well as high-level Gaussian-3 (G3)[12] and Weizmann-1 (W1)[13,14] computational methods. The latter two approaches are well-described and typically have accuracies of 1−2 kcal mol^{-1} for energetic quantities. They are also in good accord with each other, so only the W1 values are given in the text, and the G3 values are provided in the Supporting Information. Reaction energies such as heats of hydrogenation ($\Delta H^\circ_{H_2}$) and their relationship to E_π are also discussed.

■ RESULTS AND DISCUSSION

Carbon−Carbon π-Bond Energies. Two operational definitions for carbon−carbon π-bond dissociation energies are commonly employed. One makes use of the activation energy for the rotation about a carbon−carbon double bond, since in the transition structure the two p-orbitals on adjacent carbon centers are twisted (i.e., orthogonal) to one another and do not overlap.[2,15,16] This led Rabinovitch et al. to measure the interconversion rates of *cis* and *trans*-1,2-dideuterioethene as a function of temperature (eq 2), and an activation energy of 65.0



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± 1.2 kcal mol^{-1} was obtained by using the Arrhenius equation.[17,18] This is the origin of the commonly cited 65 kcal mol^{-1} carbon−carbon π-bond energy.

A more general and broadly applicable definition championed by Benson defines the π-bond strength as the difference in sequential H−X BDEs on adjacent atoms in a symmetrical compound where the two H−X bonds are equivalent.[8,19,20] For example, the C=C π-bond energy for ethene is obtained from the difference between the C−H BDE of ethane (BDE1) and that for ethyl radical at the β-carbon (BDE2). This definition assumes that the latter BDE is reduced from the former value

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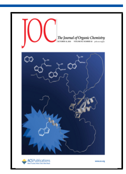

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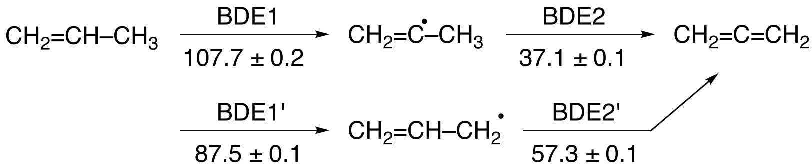
Scheme 1. 1,2-Propadiene π-Bond Energy Determination, Where All Values Are Given in kcal mol^{-1}.



E_π = BDE1 – BDE2' = BDE1' – BDE2 = 50.4 ± 0.2 kcal mol^{-1}

Note: BDE1 – BDE2 = 70.6 ± 0.2, BDE1' – BDE2' = 30.2 ± 0.1, and (70.6 ± 0.2 + 30.2 ± 0.1)/2 = 50.4 ± 0.2 kcal mol^{-1}

only by the π-bond strength. Experimental heats of formation for $H^\bullet$, $CH_3CH_2^\bullet$, and $CH_2{=}CH_2$ enable one to derive BDE1 = 101.0 ± 0.1, BDE2 = 35.8 ± 0.1, and a π-bond energy of 65.2 ± 0.1 kcal mol^{-1} for ethene (eq 3).[11] This value is the same as that obtained from the rotation barrier for ethene and is well reproduced by W1 computations, which give E_π = 65.4 kcal mol^{-1} using eq 3. They also corroborate this value using the singlet−triplet (S−T) gap (66.0 kcal mol^{-1}) as an estimate for the rotational barrier since triplet ethene has a fully twisted D_{2d} geometry.[2,16]

$$CH_3CH_2{-}H \xrightarrow{\text{BDE1 = 101.0 ± 0.1 kcal mol}^{-1}} CH_3CH_2^\bullet + H^\bullet \tag{3a}$$

$$CH_3CH_2^\bullet \xrightarrow{\text{BDE2 = 35.8 ± 0.1 kcal mol}^{-1}} CH_2{=}CH_2 + H^\bullet \tag{3b}$$

$$E_\pi = \text{BDE1} - \text{BDE2} = 65.2 \pm 0.1 \text{ kcal mol}^{-1}$$
$$(\pi\text{-bond energy})$$

The π-bond strength for the carbon−carbon triple bond of ethyne cannot be determined from its rotational barrier since the molecule is linear. Benson's approach, however, can be used in a similar manner to that for ethene. In this case, the C−H BDEs for ethene and vinyl radical are used as shown in eq 4 to obtain E_π = 75.0 ± 0.4 kcal mol^{-1}. This π-bond is stronger than for ethene by 9.8 kcal mol^{-1}, a result of the different hybridizations in ethyne (sp) and ethene (sp^2) leading to a shorter carbon−carbon bond distance (i.e., 1.20 vs 1.34 Å)[21] and more extensive overlap of the p-orbitals in the former compound. This does not mean that ethyne is more stable than ethene with

$$CH_2{=}CH{-}H \xrightarrow{\text{BDE1 = 110.6 ± 0.1 kcal mol}^{-1}} CH_2{=}CH^\bullet + H^\bullet \tag{4a}$$

$$CH_2{=}CH^\bullet \xrightarrow{\text{BDE2 = 35.6 ± 0.1 kcal mol}^{-1}} HC{\equiv}CH + H^\bullet \tag{4b}$$

$$E_\pi = \text{BDE1} - \text{BDE2} = 75.0 \pm 0.1 \text{ kcal mol}^{-1}$$

respect to the elements. In fact, the presence of the additional π-bond in the former compound makes it less stable (i.e., ΔH°_f (HC≡CH) = 54.57 ± 0.03 and ΔH°_f ($CH_2{=}CH_2$) = 12.52 ± 0.03 kcal mol^{-1}).[11] This is reflected in their heats of hydrogenation, which are 42.1 and 32.6 kcal mol^{-1}, respectively (eqs 5 and 6). This could be considered surprising since ethyne has a stronger π-bond than ethene and yet liberates more energy upon the addition of H_2. This paradoxical result arises

$$HC{\equiv}CH + H_2 \xrightarrow[\text{42.1 kcal mol}^{-1}]{-\Delta H^\circ_{rxn}=\Delta H^\circ_{H_2}} CH_2{=}CH_2 \tag{5}$$

$$CH_2{=}CH_2 + H_2 \xrightarrow[\text{32.6 kcal mol}^{-1}]{\Delta H^\circ_{H_2}=} CH_3CH_3 \tag{6}$$

because carbon−carbon π-bond strengths cannot be directly equated with heats of hydrogenation.[21] Two new C−H bonds are formed upon addition of H_2 across a π-bond and the BDE of H_2 is lost. These energetic quantities all need to be considered as illustrated for ethyne to ethene (eq 7) and ethene to ethane (eq 8). That is, ethyne gives off more energy than ethene upon the addition of one equivalent of H_2 because it forms two stronger sp^2 C−H bonds that offset the difference in the π-bond strengths.

$$\underset{(42.1)}{\Delta H^\circ_{H_2}(HC{\equiv}CH)} = \underset{2\times(110.6)}{2 \times \text{BDE}(CH_2{=}CH{-}H)} - \underset{(104.2)}{\text{BDE}(H{-}H)} - \underset{(75.0\text{ kcal mol}^{-1})}{E_\pi(HC{\equiv}CH)} \tag{7}$$

$$\underset{(32.6)}{\Delta H^\circ_{H_2}(CH_2{=}CH_2)} = \underset{2\times(101.0)}{2 \times \text{BDE}(CH_3CH_2{-}H)} - \underset{(104.2)}{\text{BDE}(H{-}H)} - \underset{(65.2\text{ kcal mol}^{-1})}{E_\pi(CH_2{=}CH_2)} \tag{8}$$

For nonsymmetric compounds a complication arises when determining π-bond energies using Benson's approach because the vicinal H−X bonds are different, and two sequential pathways can be written. For example, to obtain the π-bond energy of 1,2-propadiene (also known as allene, $CH_2{=}C{=}CH_2$), one starts with its hydrogenated product (i.e., $CH_3CH{=}CH_2$) as illustrated in Scheme 1. There are two independent pathways for forming 1,2-propadiene. These involve either cleavage of the internal sp^2 C−H bond first (BDE1) followed by the methyl C−H bond (BDE2), or cleavage of a methyl hydrogen (BDE1′) followed by the sp^2 C−H bond (BDE2′). These two pathways lead to different values for E_π, which is unsatisfactory because thermodynamic quantities need to be pathway independent.

Recognizing this issue, Benson more broadly defined the π-bond energy to address symmetric and nonsymmetric compounds alike. This is done by taking the difference in H−X bond strengths at a given site where the vicinal atom has an attached hydrogen atom or is a radical center.[19,20] Due to Hess's law, both pathways (i.e., BDE1−BDE2′ and BDE1′−BDE2 as illustrated in Scheme 1) now afford the same result. This more generalized definition for E_π also assumes that the second H−X BDE is reduced just by the π-bond strength when the adjacent atom is a radical center and is mathematically equivalent to taking the average of BDE1−BDE2 and BDE1′−BDE2′. The resulting π-bond energy for 1,2-propadiene is 50.4 ± 0.2 kcal mol^{-1} and is well reproduced by W1 calculations which give 50.7 kcal mol^{-1} and a computed S−T gap of 52.0 kcal mol^{-1}. This 15 kcal mol^{-1} reduction in E_π relative to ethene is not surprising because a resonance-stabilized radical center is formed upon rotation of one of the CH_2 groups in 1,2-propadiene by 90° to form a planar diradical species.

It is less intuitive that 1-propyne (E_π = 75.1 ± 0.2 kcal mol^{-1}) has a 25 kcal mol^{-1} stronger π-bond than 1,2-propadiene especially since their heats of hydrogenation differ by only 1.1 ± 0.3 kcal mol^{-1}. It is important to remember, however, that π-bond strengths are not independent of other molecular interactions and this large difference is primarily the result of

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the 23.7 ± 0.2 kcal mol^{-1} difference between the sp^3 CH_3 and sp^2 CH_2 C−H BDEs in propene as illustrated in eqs 9 and 10.

$$\begin{array}{llllll} E_\pi(CH_2{=}C{=}CH_2) = & BDE(CH_2{=}CHCH_2{-}H) + & BDE(CH_2{=}\overset{H}{C}CH_3) - & BDE(H{-}H) - & \Delta H^\circ_{H2}(CH_2{=}C{=}CH_2) & (9)\\ 50.4 & 87.5 & 107.7 & 104.2 & 40.6\ \text{kcal mol}^{-1} & \end{array}$$

$$\begin{array}{llllll} E_\pi(CH_3C{\equiv}CH) = & BDE(CH_3CH{=}CH{-}H) + & BDE(CH_2{=}\overset{H}{C}CH_3) - & BDE(H{-}H) - & \Delta H^\circ_{H2}(CH_3C{\equiv}CH) & (10)\\ 75.1 & 111.2 & 107.7 & 104.2 & 39.6\ \text{kcal mol}^{-1} & \end{array}$$

1,3-Butadiene is stabilized by conjugation but has a weak π-bond energy of 55.1 ± 0.3 kcal mol^{-1} (Scheme 2) which is consistent with the W1 value of 55.5 kcal mol^{-1} and a computed S−T gap of 56.8 kcal mol^{-1}. It is also in keeping with molecular orbital theory which correctly predicts that the highest occupied molecular orbital of 1,3-butadiene is higher in energy than that for ethene and that a stabilized allyl radical is formed upon rotation of one of its methylene groups. Nevertheless, 1,3-butadiene is more stable than 1,2-butadiene, 1-butyne, and 2-butyne by 9−13 kcal mol^{-1} in large part because of its six strong sp^2 C−H bonds (i.e., the BDEs for the CH_2 and CH positions are 112.0 ± 0.2, and 101.3 ± 0.2 kcal mol^{-1}, respectively).

A summary of the experimental ATcT and computed W1 π-bond energies and heats of hydrogenation are provided in Table 1; the requisite C−H BDEs for obtaining the former quantities are provided in the Supporting Information. A plot of E_π versus $\Delta H^\circ_{H_2}$ was examined but not surprisingly these two quantities are not well correlated even though they are related to each other as illustrated in eqs 7−10 (i.e., the sum of the heat of hydrogenation and π-bond energy minus BDE(H_2) equals the sum of the BDEs of the two newly formed carbon−hydrogen bonds in the hydrogenated product).

Carbon−Nitrogen π-Bond Energies. Single H−X bonds increase in strength as X changes from CH_3 to NH_2 to OH (i.e., 104.9 < 107.5 < 118.9 kcal mol^{-1}).[11] This trend has been ascribed to decreasing atomic size and increasing electronegativity in going from left to right along a row in the periodic table, all of which results in shorter H−X bond distances and increased electrostatic attraction.[22] The energy gaps between the H$^\bullet$ 1s orbital and the $CH_3^\bullet$, $NH_2^\bullet$, and $OH^\bullet$ 2p orbitals change nonmonotonically, however, and follow the order: $NH_2^\bullet$ < $OH^\bullet$ < $CH_3^\bullet$. This leads to conflicting bond strengthening and weakening tendencies that become apparent when one considers H−YCH_3 BDEs, where Y = CH_2, NH, and O. These bond strengths follow the order: H−NHCH_3 (99.5) < H−CH_2CH_3 (101.0) < H−OCH_3 (105.3 kcal mol^{-1}).[11,23] Similarly, CH_3−X BDEs follow this latter trend and are CH_3−NH_2 (84.5) < CH_3−CH_3 (90.1) < CH_3−OH (92.0 kcal mol^{-1}).[11] All three N−H and C−N BDEs just noted are similar in strength to their C−H and C−C counterparts with signed and unsigned averages for the differences of −1.5 and 3.2 kcal mol^{-1}, respectively.

Table 1. Experimental and Computed Carbon−Carbon and Carbon−Nitrogen π-Bond Energies and Heats of Hydrogenation

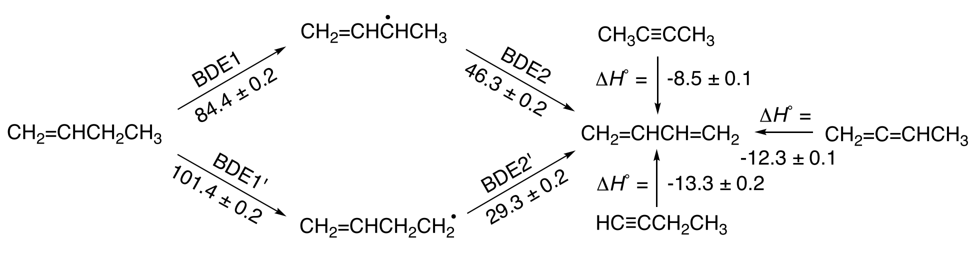
	E_π (kcal mol^{-1})		$\Delta H^\circ_{H_2}$ (kcal mol^{-1})	
compound	expt	W1	expt	W1
HC≡CH	75.0 ± 0.1	74.9	42.1 ± 0.04	42.5
CH_2═CH_2	65.2 ± 0.1	65.4	32.6 ± 0.04	33.0
CH_2═C═CH_2	50.4 ± 0.2	50.7	40.6 ± 0.1	41.0
CH_3C≡CH	75.1 ± 0.2	75.4	39.6 ± 0.1	40.0
CH_3CH═CH_2	65.6 ± 0.2	66.1	29.9 ± 0.1	30.3
CH_2═CHCH═CH_2	55.1 ± 0.3	55.5	26.5 ± 0.1	27.0
HC≡N	70.0 ± 0.2	70.2	9.8 ± 0.1	10.3
CH_2═NH	62.0 ± 0.2	62.1	26.2 ± 0.1	26.7
CH_3C≡N	73.8 ± 0.4	73.9	8.3 ± 0.2	8.3
HN═C═NH		71.3		24.5
NH_2C≡N		69.7		21.8

To compare carbon−carbon versus carbon−nitrogen π-bond strengths, E_π for CH_2═NH, HC≡N, and CH_3C≡N were determined via Benson's method and are provided in Table 1.[24] For methanimine (CH_2═NH), E_π was also obtained from W1 calculations of the S−T gap (66.5 kcal mol^{-1}), and there is reasonable accord between these two approaches and a previous determination of 63.3 kcal mol^{-1}.[2] Evidently, the π-bond strengths by these two methods are smaller for CH_2═NH than for the analogous carbon−carbon values in CH_2═CH_2, but they are similar; the differences range from 1.4−5.0 kcal mol^{-1}, which is almost the same as for the single bonds noted above (i.e., 1.5−5.6 kcal mol^{-1}). On the other hand, heats of hydrogenation of the *N*-containing compounds differ from the corresponding hydrocarbons to a much greater extent. For example, HCN has a 5.0 kcal mol^{-1} weaker π-bond than HC≡CH,[25] but $\Delta\Delta H^\circ_{H_2}$ = 32.3 kcal mol^{-1} (eq 11), which leads to an overall difference of 37.3 kcal mol^{-1}! This can be accounted for by the large C−H BDE of ethene (110.6 kcal mol^{-1}) as compared to the smaller C−H (96.0 kcal mol^{-1}) and N−H (87.9 kcal mol^{-1}) values for CH_2═NH as illustrated in eq 12.

$$HC{\equiv}CH + CH_2{=}NH \rightarrow CH_2{=}CH_2 + HC{\equiv}N \quad (11)$$

$$\begin{aligned}\Delta H^\circ_{rxn} &= \Delta H^\circ_{H_2}(C_2H_2) - \Delta H^\circ_{H_2}(HC{\equiv}N)\\ &= 42.1 - 9.8\\ &= 32.3\ \text{kcal mol}^{-1}\end{aligned}$$

Scheme 2. 1,3-Butadiene π-Bond Energy Determination and Selected C_4H_6 Isomerization Energies, Where All Values Are Given in kcal mol^{-1}.



E_π = BDE1 − BDE2' = BDE1' − BDE2 = 55.1 ± 0.3 kcal mol^{-1}

$$\underset{42.1}{\Delta H^{\circ}_{H_2}(\mathrm{HC{\equiv}CH})} - \underset{9.8}{\Delta H^{\circ}_{H_2}(\mathrm{HC{\equiv}N})} = 2 \times \underset{110.6}{\mathrm{BDE(CH_2{=}CH{-}H)}} - \underset{87.9}{\mathrm{BDE(CH_2{=}N{-}H)}} - \underset{96.0}{\mathrm{BDE(H{-}CH{=}NH)}} - \underset{70.0}{E_{\pi}(\mathrm{HC{\equiv}N})} - \underset{75.0}{E_{\pi}(\mathrm{HC{\equiv}CH})} \quad (12)$$

π-Bond strengths for diimide (HN═NH, eq 13) and molecular nitrogen (eq 14) were also determined for comparison purposes with their carbon−containing counterparts (Table 2).[26] In the former case the π-bond energy of *trans*-HN═NH was adjusted to account for resonance stabilization in HN═N$^\bullet$.[28]

Table 2. Experimental and Computed π-Bond Energies and Heats of Hydrogenation

	E_π (kcal mol^{-1})		$\Delta H^\circ_{H_2}$ (kcal mol^{-1})	
compound	expt	W1	expt	W1
CH_2═CH_2	65.2 ± 0.1	65.4	32.6 ± 0.04	33.0
CH_2═NH	62.0 ± 0.2	62.1	26.2 ± 0.1	26.7
trans-HN═NH	36.1 ± 0.3	33.7	24.5 ± 0.1	23.1
HC≡CH	75.0 ± 0.1	74.9	42.1 ± 0.04	42.5
HC≡N	70.0 ± 0.2	70.2	9.8 ± 0.1	10.3
N≡N	71.3 ± 0.2	71.2	−47.8 ± 0.1	−47.3

HN═NH is much smaller than for CH_2═CH_2 and CH_2═NH, but the heats of hydrogenation span a narrower range. Diimide's S−T gap was also computed as an estimate for the HN═NH rotation barrier, and the resulting W1 value of 42.1 kcal mol^{-1}is in accord with a weak π-bond. This is not surprising since rotation about the HN═NH bond relieves lone-pair−lone-pair electron repulsion and results in two favorable two-center−three-electron lone-pair−unpaired electron interactions (Figure 1).[27]

$$\mathrm{NH_2NH_2} \xrightarrow{\mathrm{BDE1}\,=\,82.4\,\pm\,0.2\ \mathrm{kcal\ mol^{-1}}} \mathrm{NH_2NH^\bullet} + \mathrm{H^\bullet} \quad (13a)$$

$$\mathrm{NH_2NH^\bullet} \xrightarrow{\mathrm{BDE2}\,=\,46.3\,\pm\,0.2\ \mathrm{kcal\ mol^{-1}}} trans\text{-}\mathrm{HN{=}NH} + \mathrm{H^\bullet} \quad (13b)$$

$$E_\pi = \mathrm{BDE1} - \mathrm{BDE2} = 36.1 \pm 0.3\ \mathrm{kcal\ mol^{-1}}$$

$$trans\text{-}\mathrm{HN{=}NH} \xrightarrow{\mathrm{BDE1}\,=\,63.9\,\pm\,0.1\ \mathrm{kcal\ mol^{-1}}} \mathrm{HN{=}N^\bullet} + \mathrm{H^\bullet} \quad (14a)$$

$$\mathrm{HN{=}N^\bullet} \xrightarrow{\mathrm{BDE2}\,=\,-7.5\,\pm\,0.1\ \mathrm{kcal\ mol^{-1}}} \mathrm{N{\equiv}N} + \mathrm{H^\bullet} \quad (14b)$$

$$E_\pi = \mathrm{BDE1} - \mathrm{BDE2} = 71.3 \pm 0.2\ \mathrm{kcal\ mol^{-1}}$$

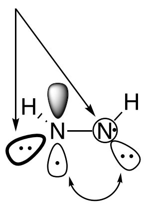


Figure 1. Twisted diimide in which both nitrogen p-orbitals overlap with the other nitrogen lone pair of electrons.

Ethyne, HCN, and N_2 have similar π-bond strengths, but very different heats of hydrogenation that range from 42.1 to −47.8 kcal mol^{-1}. This is the opposite of what was observed for the corresponding doubly bonded compounds and can be attributed almost entirely to the differences in the relevant H−X BDEs as illustrated in Scheme 3. It is worth adding that E_π = 119.7 kcal mol^{-1} has been reported for N_2,[24b] but this value seems significantly too large and arises because the N−H BDE for HN═NH was adjusted to account for resonance stabilization in HN═N$^\bullet$.[28]

Carbon−Oxygen π-Bond Energies. Oxygen is smaller in size than carbon and nitrogen, and as a result C═O bond distances are shorter than C═C and C═N bonds. This leads to better p-orbital overlap and enhances the C═O π-bond strength relative to C═C and C═N derivatives. Oxygen is also more electronegative than carbon and nitrogen, so C═O bonds are more polar and have greater Coulombic attraction which also results in stronger bonds.[29] In contrast, the oxygen 2p orbital is higher in energy than the nitrogen 2p orbital and lower in energy than the one on carbon which leads to a predicted π-bond strength order based solely on this last trend of C═N < C═O < C═C.[24] Overall, these different influences lead to carbon−carbon and carbon−nitrogen π-bonds with similar strengths, while carbon−oxygen π-bonds are generally stronger. To examine this in further detail, E_π values for a series of simply substituted carbonyl bonds were determined (Table 3).[29,30]

As anticipated given the atomic sizes, electronegativities, and orbital energies of C, N, and O, carbon−oxygen π-bonds are considerably stronger than their carbon−carbon and carbon−nitrogen counterparts. For example, the experimental CH_2═CH_2, CH_3CH═CH_2 and CH_2═NH π-bond strengths are 65.2, 65.6, and 62.0 kcal mol^{-1}, respectively whereas the corresponding values for CH_2O and CH_3CHO are 75.3 and 79.3 kcal mol^{-1}. Interestingly, the carbonyl π-bond W1 energies also span a large 33 kcal mol^{-1} range from 75 (CH_2O) to 108 ($(HO)_2CO$) kcal mol^{-1}, and the largest of these values is greater than many σ-bond energies. Electrostatics play a key factor in this regard as the Hartree−Fock atomic polar tensor (APT)[30] charges at the carbonyl carbon (q_C) with the summed hydrogen atom contributions range from 0.68 (CH_2O) to 1.76 ($(HO)_2CO$), and a plot of E_π versus q_C is linearly correlated (Figure 2). Least-squares fit of the data points affords E_π (kcal mol^{-1}) = 27.3 × q_C + 57.4, r^2 = 0.928. These results are consistent with the suggestion that carbon−oxygen double bonds be represented by two resonance structures, one with a covalent carbon−oxygen double bond (R_2C═O) and a dipolar form (R_2C^+−O^-) for the other (Scheme 4).[31] They also account for the large substituent effects observed at the carbonyl carbon atom, something that is not found for carbon−carbon double bonds.

The W1 heats of hydrogenation of the carbonyl-containing compounds listed in Table 3 span a 23 kcal mol^{-1} range, which also can be rationalized in part by electrostatic effects. A plot of $\Delta H^\circ_{H_2}$ versus q_C (Figure 3), however, has more scatter than in Figure 2, and a linear least-squares analysis affords $\Delta H^\circ_{H_2}$ (kcal mol^{-1}) = −19.0 × q_C + 32.1, r^2 = 0.803.

■ CONCLUSIONS

The origin of π-bond energies is presented and some representative carbon−carbon, carbon−nitrogen, carbon−oxygen and nitrogen−nitrogen values are given. In general, E_π for the former two compounds are quite similar whereas carbon−oxygen values are significantly stronger. As for nitrogen−nitrogen π-bonds, HN═NH is found to be much weaker than C═C and C═N values whereas E_π for N≡N is like those for HC≡CH and HC≡N. The (dis)connection between E_π and heats of hydrogenation are also discussed.

■ COMPUTATIONS

All G3 and W1 computations were carried out using the Gaussian 16[32] software package using the G3 and W1RO

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Scheme 3. Relationships between E_π, $\Delta H^\circ_{H_2}$, and BDEs for HC≡CH, HC ≡ N, and N ≡ N, Where All the Energies Are Given in kcal mol^{-1}

$$\Delta H^\circ_{H_2}(HC{\equiv}CH) = 2 \times BDE(CH_2{=}CH{-}H) - BDE(H_2) - E_\pi(HC{\equiv}CH)$$
$$42.1 = 2(110.6) - 104.2 - 75.0$$

$$\Delta H^\circ_{H_2}(HC{\equiv}N) = BDE(H{-}CH{=}NH) + BDE(CH_2{=}N{-}H) - BDE(H_2) - E_\pi(HC{\equiv}N)$$
$$9.8 = 96.0 + 87.9 - 104.2 - 70.0$$

$$E_\pi(N{\equiv}N) + \Delta H^\circ_{H_2}(N{\equiv}N) = 2 \times BDE(H{-}N{=}NH) - BDE(H_2) - E_\pi(N{\equiv}N)$$
$$-47.8 = 2(63.9) - 104.2 - 71.3$$

Table 3. Experimental and Computed C═O π-Bond Energies and Carbonyl Carbon Atomic Polar Tensor (APT) Charges (q_C)

	E_π (kcal mol^{-1})		q_C (APT)[a]	$\Delta H^\circ_{H_2}$ (kcal mol^{-1})	
compound	expt	W1	HF/6-31G(d)	expt	W1
CH_2O	75.3 ± 0.1	75.0	0.68	21.9 ± 0.04	22.4
CH_3CHO	79.3 ± 0.2	79.1	0.76	16.6 ± 0.1	17.1
CH_3COCH_3	83.5 ± 0.4	82.8	0.89	13.3 ± 0.1	14.0
$HCONH_2$		94.6	1.25		2.5
HCO_2H		94.6	1.31	3.6 ± 0.2	4.0
HCOF		89.0	1.35		10.6
CH_3COF		91.8	1.36		8.8
$(HO)_2CO$		107.5	1.76		−0.1

[a]See ref 30.

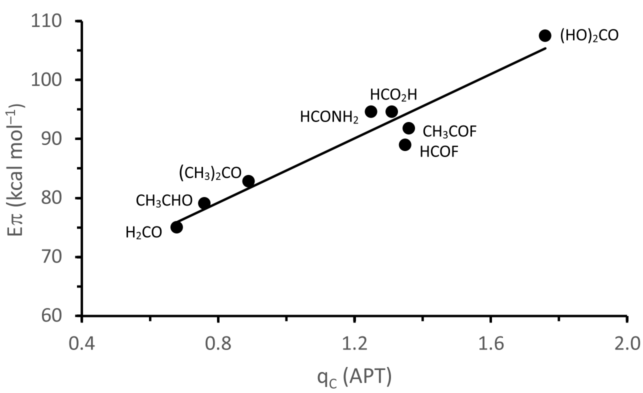


Figure 2. Plot of W1 carbonyl π-bond energies versus HF/6-31G(d) APT atomic charges at the carbonyl carbon.

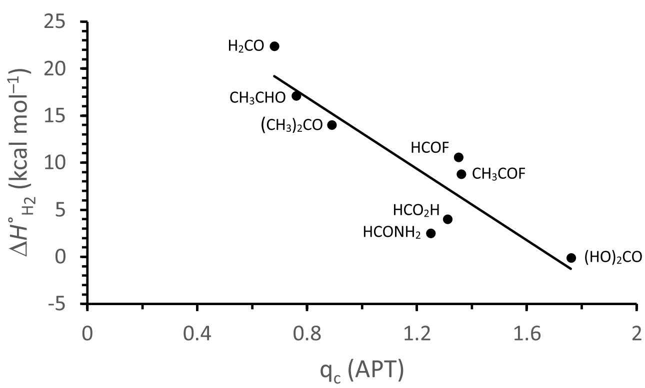
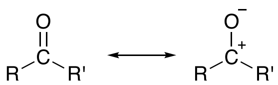


Figure 3. Plot of W1 carbonyl heats of hydrogenation versus HF/6-31G(d) APT atomic charges at the carbonyl carbon.

Scheme 4. Resonance Structures for Carbonyl-Containing Compounds That Account for the Large Impact of Substituents and Their Common Electrophilic Reactivity



keywords. For homoallyl radical, a G3B3[33] energy was determined instead of the G3 value. The calculations were carried out at the Minnesota Supercomputing Institute for Advanced Computational Research or on a MacIntosh computer with the assistance of GaussView 6.[34] APT[24] charges are provided in the output files for the G3 computations and the values with the hydrogen atom contributions summed into the heavy atoms were used in this work.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.4c01925.

Computed structures, energies, bond dissociation energies, π-bond energies and heats of hydrogenation, and the complete citation to ref 32 (PDF)

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Notes

The author declares no competing financial interest.

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(23) Hyperconjugation of the radical center by the adjacent C−H bonds also help to explain this trend since electronegativity makes O a better one-electron acceptor than NH and NH a better acceptor than CH_2.

(24) For previous determinations, see ref 2 and (a) Bonačić-Koutecký, V.; Michl, J. Photochemical *syn-anti* Isomerization of a Schiff Base: A Two-Dimensional Description of a Conical Intersection in Formaldimine. *Theor. Chim. Acta* **1985**, *68*, 45−55. (b) Borden, W. T. Why Are Addition Reactions to N_2 Thermodynamically Unfavorable? *J. Phys. Chem. A* **2017**, *121*, 1140−1144.

(25) E_π (HCN) = 84.6 kcal mol^{-1} is given in ref 24b, and this larger value is the result of using a resonance-corrected BDE.

(26) Also see, ref 2 and 24b.

(27) For a discussion about this type of stabilization, see: Alabugin, I.; Kuhn, L. *Oxygen: The Key to Stereoelectronic Control in Chemistry*; American Chemical Society, Washington, D. C., 2023; DOI: 10.1021/acsinfocus.7e7009).

(28) This large π-bond energy was justified by noting that the N≡N bond distance is 0.1 Å shorter than the C≡C bond length in ethyne. However, this π-bond energy is larger than most σ-bond strengths and CCSD(T)/aug-cc-pVTZ//B3LYP/cc-pVTZ calculations indicate that the energy of N_2 only increases by 10 kcal mol^{-1} when the N≡N bond distance is elongated by 0.1 Å. Presumably, this is because of unfavorable lone-pair−lone-pair electrostatic interactions that increase when the N≡N distance is reduced. Finally, it is worth adding that using the approach described in ref 23b for *trans*-HN═NH affords E_π = 70.3 kcal mol^{-1}, and this value is nearly 30 kcal mol^{-1} larger than the computed W1 S−T gap for diimide of 42.1 kcal mol^{-1}.

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