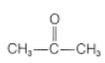
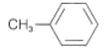
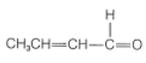
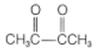


1.1.2: Bond Lengths and Double-Bond Character

Bond lengths frequently are cited as evidence for, or against, electron delocalization, although some caution should be exercised in this respect. For instance, if the hybrid structure of benzene is considered to be represented by the two possible Kekule structures, then each carbon-carbon bond should be halfway between a single bond and a double bond. In other words, each should possess 50% *double-bond character*. We then may expect the carbon-carbon bond lengths for benzene to be the average of single- and double-bond lengths. However, the average of the C—C bond in ethane (1.534 Å) and in ethene (1.337 Å) is 1.436 Å, which does not agree well with the measured C—C bond distance for benzene of 1.397 Å. The discrepancy lies largely in the assumption inherent in this crude calculation that, in the absence of resonance, all C—C single bonds are equal to 1.534 Å. Clearly, this is not a valid assumption because, as we have seen, bond energies depend upon environment, and because the energy of a bond depends upon its length (see Figure 21-1), bond lengths also must vary with environment. This can be seen from the data in Table 21-3, which gives the carbon-carbon *single* bond lengths for several compounds. The single bonds shorten as the other bonds to carbon become progressively unsaturated, that is, as the hybridization of carbon changes from sp^3 to sp . Admittedly, some of this shortening may be ascribed to resonance, but not all.

Table 21-3: Carbon-Carbon Single-Bond Distances (Å)

Bond type	Bond length	Bond type	Bond length
sp^3-sp^3		sp^3-sp^2	
CH ₃ —CH ₃	1.534	CH ₃ —CH=CH—CH ₃	1.54
CH ₃ —CH ₂ —CH ₃	1.54		1.52
diamond	1.544		1.52
sp^3-sp		sp^2-sp^2	
CH ₃ —C≡CH	1.459	CH ₂ =CH—CH=CH ₂	1.483
CH ₃ —C≡N	1.458		1.46
CH ₃ —C≡C—C≡N	1.458		1.47
sp^2-sp		$sp-sp$	
CH ₂ =CH—C≡CH	1.446	HC≡C—C≡CH	1.379
CH ₂ =CH—C≡N	1.426	HC≡C—C≡N	1.378
O=CH—C≡CH	1.445	N≡C—C≡N	1.380

If we take 1.48 Å as a reasonable C—C bond distance between two sp^2 -hybridized carbons and 1.34 Å for C=C bonds (see Table 2-1), the average is 1.41 Å, which is not much different from the 1.40 Å for the carbon-carbon bonds in benzene.

1.1.2.1: Contributors and Attributions

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