# Organic and Biological Chemistry

## Ground States of Conjugated Molecules. XV.[1] Bond Localization and Resonance Energies in Compounds Containing Nitrogen or Oxygen[2]

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**Abstract:** The heats of formation of, and bond lengths in, a number of classical conjugated molecules containing nitrogen or oxygen have been calculated by the method of part XII of this series. The results imply that the bonds in compounds of this type can be regarded as localized. Using the bond energies deduced in this way, resonance energies are calculated for a number of aromatic, and potentially aromatic, compounds containing nitrogen or oxygen.

Previous papers of this series[5] have shown that the heats of atomization of classical polyenes, calculated by our semiempirical $\pi$ SCF MO procedure,[5,6] can be reproduced very accurately by sums of "polyene" bond energies, the latest[6] estimates of these being those of eq 1. Since our procedure has been shown[6] to give

$$\begin{aligned} E_{\mathrm{C-C}} &= 4.3499 \text{ eV} \\ E_{\mathrm{C=C}} &= 5.5378 \text{ eV} \qquad (1) \\ E_{\mathrm{CH}} &= 4.4375 \text{ eV} \end{aligned}$$

very good estimates of heats of atomization of conjugated hydrocarbons of all types, this provides strong evidence that the bonds in polyenes can be regarded as localized.[7]

The bond energy of the polyene single bond is considerably greater (by 0.409 eV or 9.43 kcal/mol) than that estimated[6] for a "pure" $\sigma$ bond between sp$^2$-hybridized carbon atoms; the polyene single bonds evidently have strong $\pi$ components. Since, however, the contribution of $\pi$ bonding seems to be constant in classical polyenes of all types,[5c,6] this does not affect the conclusion that the bonds in such polyenes are localized.[7] The polyene double bond energy on the other hand is only a little less (by 0.02 eV or 0.5 kcal/mol) than the value estimated[6] for a "pure" C=C double bond.

Accepting the conclusion that the bonds in classical polyenes are localized, we are then[5c,7] led to a simple definition of resonance energy, as the difference in heat of atomization between a given conjugated hydrocarbon and the value calculated for a corresponding classical polyene by summing appropriate bond energies (eq 1). This definition of resonance energy is superior to others that have been proposed, for two reasons. First, the quantity in which chemists are primarily interested concerning compounds such as benzene is not their stability relative to some idealized structure with "pure" single and double bonds, but rather their stability relative to open-chain analogs. Since the latter are classical polyenes (*e.g.*, 1,3,5-hexatriene in the case of benzene), the quantity in question is precisely the one we have defined as resonance energy. Secondly, our definition is independent of theory, for the polyene bond energies could be, and indeed should be, estimated from thermochemical data. We calculated them theoretically (eq 1) only because such data are as yet lacking. A definition in terms of "pure" single and double bonds would necessarily be linked to some theoretical estimate of the corresponding bond energies given that they cannot be determined experimentally.

The success of this definition of resonance energy rests of course on the apparent additivity of bond energies in classical conjugated hydrocarbons; it is obviously of considerable interest to see whether a similar additivity holds in the case of compounds containing other elements, in particular nitrogen and oxygen. Here again the problem cannot be approached empirically for lack of suitable thermochemical data; however the $\pi$ SCF MO procedure[5,6] has been successfully extended to conjugated compounds containing nitrogen and oxygen,[8] and we have accordingly used it to study bond localization in classical compounds of this type.

### Theoretical Method

The calculations were carried out by the procedure described in part XII[8] of this series, in which allowance is made for the effects of polarity in the $\sigma$ components of bonds and for the variations in the values of two-center integrals for pairs of directly linked atoms, due to

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(1) (a) Part XIII: M. J. S. Dewar and T. Morita, *J. Amer. Chem. Soc.*, **91**, 802 (1969); (b) part XIV: M. J. S. Dewar and N. Trinajstić, in preparation.

(2) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(3) Robert A. Welch Postdoctoral Fellow.

(4) Robert A. Welch Postdoctoral Fellow. On leave of absence from The Rudjer Bošković Institute, Zagreb, Croatia, Yugoslavia.

(5) (a) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965); (b) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965); (c) *ibid.*, **87**, 692 (1965).

(6) M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969).

(7) (a) M. J. S. Dewar, *Tetrahedron, Suppl.*, **8**, 75 (1966); (b) M. J. S. Dewar, *Chem. Eng. News*, **43**, 86 (Jan, 11, 1965).

(8) M. J. S. Dewar and T. Morita, *J. Amer. Chem. Soc.*, **91**, 796 (1969).

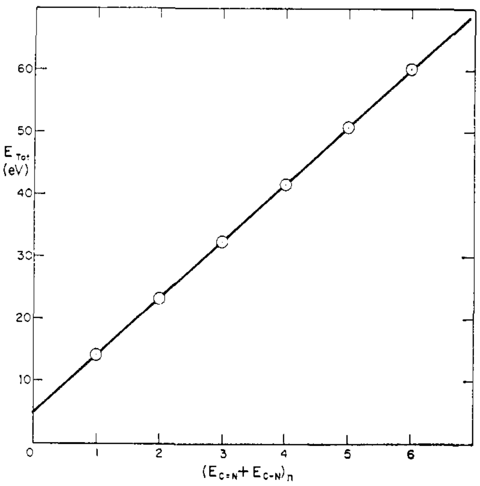

Figure 1. Plot of $E$(CN) *vs.* $n$ for polyazopolyenes (I).

variations in bond length (variable $\beta$ procedure[5b]). The lengths of the bonds are recalculated at each step in the SCF iterative procedure, assuming a linear relation between bond order and bond length, and the corresponding two-center integrals are then recalculated accordingly; the integrals between nonadjacent pairs of atoms are, however, assumed to retain the values corresponding to the geometry assumed initially. If the final bond lengths differ significantly from those assumed initially, the results may be affected by failure to allow for corresponding changes in the nonbonded interactions. In cases where this was so we accordingly repeated the calculation, using an initial geometry corresponding to the final bond lengths from the previous calculation; in practice, the results of this second calculation never differed significantly from those of the first, so the neglect of change in nonbonded interactions is apparently unimportant. A similar conclusion was reached for the systems previously studied by this procedure.[5,7]

## Effect of Electronegativity on Bond Energy

It is now generally accepted that the strengths of bonds formed by a given atom must to some extent depend on its formal charge, since changes in formal charges lead to changes in electronegativity.[9] Indeed, the effect of the polarity of $\sigma$ bonds had to be taken into account in our $\pi$ treatment[8] of conjugated molecules containing nitrogen or oxygen by making appropriate changes in the corresponding valence-state ionization potentials. In discussing the additivity of bond energies in such molecules, one must be prepared to allow for this effect; thus, the properties of a given CN bond are bound to be different in cases where carbon is adjacent to another carbon from those where it is adjacent to another heteroatom. In developing a set of bond energies we must be prepared to use different values for the two cases, just as we use different values for bonds formed by carbon in different states of hybridization.[10]

## Bond Localization in Conjugated Compounds of Nitrogen and Oxygen; Bond Energies

The procedure used to determine the bond energies of localized bonds was similar to that used in part XI[6] for polyenes. The first case considered was that of the polyazapolyenes (I). If the heats of formation of such

$$H_2C{=}N(CH{=}N)_nH$$

I

molecules can be expressed as sums of bond energies, the total CN bond energy, $E$(CN), should be given by eq 2, where $n$ is the number of C–N bonds in the classical structure (I) and $E_{C-N}$ and $E_{C=N}$ are the corresponding energies. A plot of $E$(CN) *vs.* $n$ should then be a straight line of slope $E_{C-N} + E_{C=N}$ and intercept $E_{C=N}$.

$$E(CN) = n(E_{C-N} + E_{C=N}) + E_{C=N} \tag{2}$$

Figure 1 shows the corresponding plot for $n$ = 1–6, $E$(CN) being calculated by our $\pi$ SCF MO method.[8] The points obviously lie very close indeed to a straight line, the slope and intercept of which lead to the following values for the bond energies. The value for $E_{C=N}$

$$\begin{aligned} E_{C-N} &= 4.1800 \text{ eV} \\ E_{C=N} &= 4.9950 \text{ eV} \end{aligned} \tag{3}$$

is very little less than that (5.177 eV) estimated[8] for a "pure" C=N bond, while the value for $E_{C-N}$ is considerably greater than that (3.346 eV) estimated[8] for a "pure" C—N bond. Similar relationships held[6] for the corresponding bond energies in polyenes and an explanation has been given in terms of perturbation theory (PMO method).[11]

The localization of bonds in I is further indicated by their lengths (Table I). While the lengths of "single" and "double" bonds vary more than in the polyenes,[6] the over-all variations are still quite small. Note that the molecules are predicted to be symmetrical, the length of a bond depending only on its distance from

Table I. Bond Lengths and Energies of Polyazapolyenes (I)

| $n$ in N=C-(CN)$_n$ | Calculated bond lengths, Å[a] Single bonds | Double bonds | $E$(CN), eV | $\Delta H_a$, eV |
|---|---|---|---|---|
| 1 | 1.404 | 1.286, 1.286 | 14.221 | 27.534 |
| 2 | 1.400, 1.400 | 1.288, 1.297, 1.288 | 23.328 | 41.078 |
| 3 | 1.398, 1.394, 1.398 | 1.290, 1.300 1.300, 1.290 | 32.480 | 54.667 |
| 4 | 1.397, 1.390 1.390, 1.397 | 1.291, 1.303, 1.305, 1.303, 1.291 | 41.662 | 68.287 |
| 5 | 1.396, 1.388, 1.386, 1.388, 1.396 | 1.291, 1.304, 1.309, 1.309, 1.304, 1.291 | 50.867 | 81.929 |
| 6 | 1.395, 1.387, 1.383, 1.383, 1.387, 1.395 | 1.292, 1.306, 1.311, 1.312, 1.311, 1.306, 1.292 | 60.087 | 95.587 |

[a] In order, starting from the terminal nitrogen atom in I.

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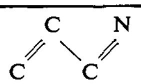
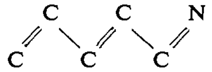
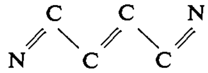
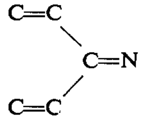
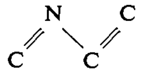
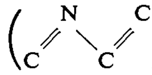
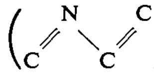
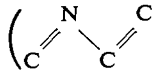
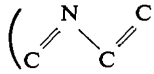
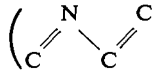
[9] See A. Buraway in "Contribution to the Study of Molecular Structure," V. Henri Comm. Vol., Desoer, Liège, 1948, p 73; *Trans. Faraday Soc.*, **40**, 537 (1944).

[10] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); **11**, 96 (1960).

[11] See ref 7a. The difference in $\pi$-bond energy between a classical polyene and a corresponding number of ethylene units is a second-order perturbation which can be absorbed into the empirical C–C "polyene" bond energies of the "single" bonds linking C=C units in the polyene.

**Table II.** Bond Lengths and Energies of Miscellaneous Azapolyenes

| Molecule | Calculated bond lengths, Å[a] Single bonds | Calculated bond lengths, Å[a] Double bonds | $E$(CN),[b] eV | $E'$(CN),[c] eV | $\Delta H_a$, eV |
|---|---|---|---|---|---|
|  | 1.466 | 1.344, 1.285 | 15.064 | 15.053 | 32.814 |
|  | 1.466, 1.464 | 1.344, 1.351,<br>1 285 | 24.954 | 24.941 | 51.579 |
|  | 1.467 | 1.283, 1.350 | 24.527 | 24.568 | 42.277 |
|  | 1.468 | 1.344, 1.290 | 24.938 | 24.941 | 51.563 |
|  | 1.406 | 1.284, 1.343 | 14.469 | 14.537 | 36.657 |
|  | 1.403, 1.460,<br>1.404 | 1.286, 1.352,<br>1.293, 1.344 | 33.346 | 33.425 | 68.846 |
|  | 1.402, 1.457,<br>1.399, 1.457,<br>1.403 | 1.287, 1.353,<br>1.297, 1.354,<br>1.295, 1.344 | 52.264 | 52.312 | 101.077 |
|  | 1.402, 1.456,<br>1.398, 1.456,<br>1.398, 1.456,<br>1.403 | 1.287, 1.354,<br>1.299, 1.356,<br>1.299, 1.356,<br>1.295, 1.344 | 71.202 | 71.200 | 133.327 |
|  | *d* | *d* | 90.150 | 90.087 | 165.588 |
|  | *d* | *d* | 109.105 | 108.975 | 197.855 |

[a] In order, starting from the left-hand end of the formula in column 1; bond lengths which must be identical from symmetry are given once only. [b] Calculated by the $\pi$ SCF MO method.[8] [c] From bond energies in eq 1, 3, and 4. [d] Bond lengths identical (± 0.001 Å) with those in tetramer.

an end of the molecule, not on which end (—C═N or —N═C). Table I also lists values for $E$(CN) and for the heat of atomization ($\Delta H_a$) of the polyene analog derived from I by adding $n + 4$ atoms of hydrogen, using the CH and NH bond energies from parts XI[6] and XII.[8]

In order to see whether the CN bond energies would be affected by the atom adjacent to carbon, we also calculated $E$(CN) for a number of azapolyenes containing the unit CCN; the results are shown in Table II, together with bond lengths and heats of atomization ($\Delta H_a$) of the corresponding azapolyenes. The bond lengths are very similar to those of part XI[6] and Table I, but the values of $E$(CN) lead to different values ($E'_{\text{C-N}}$ and $E'_{\text{C=N}}$) for the single and double bond energies (eq 4). The values of $E$(CN) calculated with the

$$E'_{\text{C-N}} = 3.8343 \text{ eV}$$
$$E'_{\text{C=N}} = 5.1654 \text{ eV} \tag{4}$$

bond energies of eq 1, 3, and 4 are also shown in Table II ($E'$(CN)).

The bond energies of the bonds formed by unsaturated carbon to amine-type nitrogen might be expected to vary greatly, since compounds of this type are isoconjugate with carbanions and so might be expected to have large and variable resonance energies. The data in Table III lead to a value for the corresponding bond energy ($E''_{\text{C-N}}$) which is actually *less* than the

$$E''_{\text{C-N}} = 3.5903 \text{ eV} \tag{5}$$

values ($E_{\text{C-N}}$, $E'_{\text{C-N}}$) for even systems. Apparently bonds formed by "pyrrole-type" nitrogen, in conjugated systems otherwise containing only carbon, are localized.

**Table III.** Bond Lengths and Energies for Vinylamines

| Compound | Bond lengths, Å C═C | Bond lengths, Å C—N | $E$(CN),[a] eV | $E'$-(CN),[b] eV | $\Delta H_a$, eV |
|---|---|---|---|---|---|
| $H_2C{=}CHNH_2$ | 1.341 | 1.414 | 9.111 | 9.128 | 30.507 |
| $(H_2C{=}CH)_2NH$ | 1.341 | 1.414 | 18.256 | 18.256 | 48.923 |
| $(H_2C{=}CH)_3N$ | 1.341 | 1.414 | 27.437 | 27.384 | 67.375 |

[a] Calculated by the $\pi$ SCF MO method.[8] [b] From bond energies in eq 1 and 5.

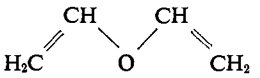
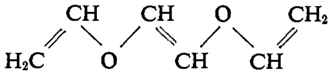
The bond energies for C—O and C═O were found likewise from the results listed in Tables IV and V. Again, the calculated values of the total carbon–carbon/carbon–oxygen bond energy, $E$(CO), can be expressed quite well as sums of bond energies and the bond lengths also indicate bond localization in the compounds studied. The bond energies derived in this way are

$$E_{\text{C-O}} = 4.1594 \text{ eV}$$
$$E_{\text{C=O}} = 7.1575 \text{ eV} \tag{6}$$

## Resonance Energies of Some Nitrogen and Oxygen Compounds

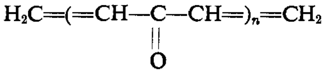
In cases where classical conjugated molecules can be regarded[7] as having localized bonds, a simple defini-

Table IV. Bond Lengths and Energies for Ethers

| Compound | Calculated bond lengths, A[a] C=C | C—O | $E$(CO),[b] eV | $E'$(CO),[c] eV | $\Delta H_a$, eV |
|---|---|---|---|---|---|
|  | 1.338 | 1.387 | 19.405 | 19.394 | 46.030 |
|  | 1.338 | 1.387 | 33.245 | 33.251 | 68.749 |
| $H_2C{=}({=}CH{-}O{-}CH{=})_3{=}CH_2$ | 1.338 | 1.387 | 47.083 | 47.108 | 91.458 |

[a] C=C and C—O bond lengths identical within ±0.001 A. [b] From π SCF MO method.[8] [c] From bond energies in eq 1 and 6.

Table V. Bond Lengths and Energies in Ketones

| $n$ in  $H_2C{=}({=}CH{-}C({=}O){-}CH{=})_n{=}CH_2$ | Calculated bond lengths, A[a] C=C | C—C | C=O | $E$(CO),[b] eV | $E'$(CO),[c] eV | $\Delta H_a$, eV |
|---|---|---|---|---|---|---|
| 1 | 1.345 | 1.466 | 1.259 | 26.974 | 26.933 | 53.599 |
| 2 | 1.346 | 1.465 | 1.258 | 48.312 | 48.328 | 83.812 |
| | 1.348 | 1.470 | | | | |
| 3 | 1.346 | 1.465 | 1.257 | 69.624 | 69.723 | 113.999 |
| | 1.349 | 1.470 | 1.256 | | | |
| | | 1.468 | | | | |

[a] In order, starting from end of molecule. [b] From π SCF MO method.[8] [c] From bond energies in eq 1 and 6.

tion of resonance energy is available[6] as the difference in heat of atomization between a given compound and the value calculated for a corresponding classical structure as a sum of bond energies. The calculations described above suggest that classical molecules containing nitrogen and oxygen are localized in our sense,[7] even in the case of ethers and amines where classical structures other than the neutral "ground state" would be zwitterionic and involve transfer of charge from nitrogen and oxygen to carbon. We have accordingly calculated the heats of atomization of a number of conjugated compounds containing nitrogen or oxygen by our π SCF MO method[8] and estimated their resonance energies ($E_R$) by comparison with heats of atomization calculated for corresponding classical structures from the bond energies of eq 1–6. The results are shown in Tables VI and VII, where the calculated heats of atomization are also compared with values estimated from thermochemical data.

Table VI. Resonance Energies ($E_R$) of Some Nitrogen Compounds

| Molecule | $\Delta H_a$ (exptl), eV | $\Delta H_a$ (calcd), eV | $E_R$, kcal/mol |
|---|---|---|---|
| Pyridine | 51.789 | 51.870 | 20.94 |
| Quinoline | 85.181 | 85.322 | 32.95 |
| Pyrimidine | 46.990 | 46.864 | 20.20 |
| Pyrazine | 46.444 | 46.272 | 14.64 |
| 1,5-Naphthyridine | | 79.985 | 31.09 |
| 1,8-Naphthyridine | | 80.162 | 27.07 |
| Quinoxaline | | 79.739 | 25.41 |
| Quinazoline | | 80.306 | 30.39 |
| Pyrrole | 44.770 | 44.768 | 8.53 |
| Aniline | 64.309 | 64.338 | 19.90 |
| α-Naphthylamine | 97.790 | 97.814 | 29.73 |
| β-Naphthylamine | 97.977 | 97.812 | 29.66 |
| Imidazole | 39.660 | 39.741 | 15.43 |
| Benzimidazole | 73.235 | 73.413 | 30.90 |

Table VII. Resonance Energies of Some Oxygen Compounds

| Molecule | $\Delta H_a$ (exptl), eV | $\Delta H_a$ (calcd), eV | $E_R$, kcal/mol |
|---|---|---|---|
| Furan | 41.519 | 41.563 | 1.59 |
| Benzofuran | | 75.376 | 20.34 |
| Dibenzofuran | 109.184 | 109.224 | 39.87 |
| Diphenyl ether | 113.835 | 113.778 | 40.54 |
| Benzaldehyde | 68.271 | 68.507 | 16.42 |
| α-Naphthylaldehyde | | 102.099 | 30.05 |
| β-Naphthylaldehyde | | 102.054 | 29.01 |
| Benzophenone | 120.983 | 121.239 | 38.79 |
| Phenol | 61.60 | 61.666 | 20.48 |
| α-Naphthol | | 95.117 | 30.83 |
| β-Naphthol | | 95.118 | 30.86 |
| Tropone | | 67.827 | 0.74 |
| Tropolone | 72.21 | 72.266 | −0.50 |
| *p*-Hydroquinone | | 66.128 | 20.43 |
| *o*-Hydroquinone | | 66.157 | 19.74 |

## Discussion

The values for $E_R$ in Table VI imply that the resonance energies of even nitrogen heteroaromatics are very similar to those for the isoconjugate hydrocarbons (*cf.*[6] benzene, 20.04 kcal/mol; naphthalene, 30.51 kcal/mol), in agreement with conclusion reached on the basis of PMO theory;[12] moreover, the resonance energies calculated for aniline, and for α- and β-naphthylamines, are if anything *less* than those for the parent hydrocarbons, confirming that the C–N bonds in such compounds are localized. The resonance energies of the compounds containing five-membered rings also seem reasonable; thus benzimidazole, with a resonance energy very similar to that of naphthalene, is a very stable system, as indicated by the thermal stability of polymers containing this ring system.[13] Note also that quinoxaline is predicted to have a lower resonance

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(12) M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3341, 3345, 3347, 3350, 3354, 3355, 3357 (1952); "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969.

(13) F. Trischler, K. Kjoller, and H. Levine, *J. Appl. Polym. Sci.*, **11**, 1325 (1967).

energy than quinazoline; while quantitative data are lacking, the nitrogen-containing ring of quinoxaline certainly seems to be more labile to hydrolysis than that of quinazoline.

The resonance energies predicted for oxygen compounds also seem to be consistent with their chemical behavior; thus the resonance energies of benzaldehyde, the hydroxybenzenes, and phenyl ketones are predicted to be not dissimilar to that of benzene, and the naphthols to that of naphthalene. The enhanced acidity of the phenols can of course be attributed to an increase in resonance energy when the group adjacent to phenyl or naphthyl is $O^-$ instead of OH, $O^-$ being much less electronegative.

On the other hand the calculated resonance energies lead to the prediction that three compounds, normally considered aromatic, in fact are not, *viz.*, furan, tropone, and tropolone. This, however, seems to be consistent with the available data.

The bond lengths in furan[14a] are very similar to those that would be predicted for a 1,3-butadiene derivative,[14b] and the classical nature of this molecule is further supported by the facility with which it undergoes Diels–Alder reactions, unlike thiophene or pyrrole. The chemical reactions of furan are also exactly what would be expected for a cyclic dienyl ether; substitution reactions take place only in cases where electrophilic attack on furan would lead to an intermediate carbonium ion that might be expected to undergo loss of a proton rather than addition, in order to avoid forming a product with eclipsed $sp^3$ carbon atoms.

The conclusions regarding tropone and tropolone are perhaps more startling, since the aromatic nature of tropolone was a presupposition of its original postulation as a component of stipitatic acid and colchicine.[15] However, most of the special properties of these compounds can be attributed to the facility with which they form symmetrical conjugate acids or bases, rather than to any special properties of the parent compounds. Thus tropone is very stable under acidic conditions, when it exists as the conjugate acid $C_7H_6OH^+$, but not under neutral or basic conditions, when it can undergo, *e.g.*, Diels–Alder reactions,[16] whereas tropolone, which can exist both as a stable conjugate acid, dihydroxytropylium, $C_7H_5(OH)_2^+$, and as a stable conjugate base, $C_7H_5O_2^-$, is stable to both acids and bases.

Further confirmation is provided by a recent structure determination for 4,5-benzotropone[17] which shows the seven-membered ring in this compound to have a classical structure, the lengths of the "single" and "double" carbon–carbon bonds being close to those in 1,3-butadiene.

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(15) M. J. S. Dewar, *Nature*, **155**, 50, 141, 479 (1945).

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# A Critical Evaluation of the Dependence of $^3J_{HH}$ Couplings on Bond Order and Bond Length in Conjugated Carbocyclic Molecules. Evidence for a Steric Effect on $^3J_{HH}$[1]

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**Abstract:** Previously proposed linear correlations between π-bond orders and the magnitudes of nmr *ortho* proton–proton spin–spin coupling constants ($^3J$) in unsaturated systems have been reinvestigated using more accurate values for the coupling constants than were available heretofore. It is shown that, although the relationship is no longer linear over the whole range of bond order, the plot is still approximately linear for aromatic systems. Deviations from linearity are shown to exhibit consistent trends, which may be rationalized in terms of steric interactions. A plot of $^3J$ *vs.* bond length is shown to be linear over the whole range of bond lengths, and the theoretical background of this correlation is discussed in terms of a simple molecular orbital theory, as well as a previously proposed valence bond treatment.

Apart from their invaluable aid in structural studies, determinations of reliable nuclear magnetic resonance (nmr) spin–spin coupling constants provide a criterion against which molecular wave functions and theoretical treatments can be tested. However, while high-resolution nuclear magnetic resonance (nmr) spectra have been recorded for more than a decade, it is only more recently, with the advent of iterative computer fitting of spectra and field-frequency locked spectrometers operating at high field strengths, that many complex spin systems have become amenable to complete analysis. In connection with another project, we had occasion to remeasure the spectra of some aromatic and olefinic compounds. In several cases we obtained vic-

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