The Synthesis and Study of Pseudoaromatic Compounds. IX. A Reevaluation of the Question of Aromatic Character in Tropones Based on Data Derived from Dipole Moment Measurements and CNDO/2 Calculations[1]

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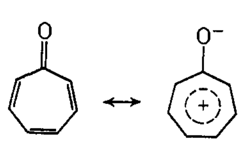
Abstract: An analysis of the dipole moments of several unsaturated ketones and aldehydes in conjunction with CNDO/2 molecular orbital calculations is presented. In general this theory is shown to calculate dipole moments of ketones and aldehydes very well, and in conjunction with other experimental evidence leads to the conclusion that the dipolar character of tropones and tropolones has been greatly overestimated and that the ground states of these systems are adequately described as polyolefinic.

Among the more interesting molecules whose ground-state electronic properties can be studied are fully unsaturated systems, and especially benzenoid and nonbenzenoid aromatic compounds. This is particularly true since recent definitions of aromaticity are dependent upon an understanding of π-electron delocalization and charge distribution in the unperturbed molecule.[3]

Tropone is generally considered to be a representative nonbenzenoid aromatic compound.[4] Although several years have elapsed since tropone was first synthesized,[5] assignment of the originally anticipated cycloheptatrienylium oxide structure **1b** as the *best* representation of tropone may still be found in the current chemical literature.[6] More commonly tropone is classified as a compound possessing aromatic character[7] as a result of a significant ground-state contribution from the cyclic delocalized resonance structure **1b**. This characterization stems primarily from the empirical resonance energy,[8] planarity,[9] diamagnetic susceptibility,[10] and dipole moment[11] of this molecule. Since tropone is an early member of a growing list of molecules which can potentially possess or have been assigned aromatic character through charge separation involving an exocyclic group,[4d,12] we believe it is of value to reinvestigate some of the theoretical and experimental premises for this classification.



1a **1b**

The somewhat ambiguous concept of π-electron delocalization is theoretical in origin and refers to the nondynamic ground-state properties of a molecule. The elucidation of this concept is dependent upon a comparison of physically measurable properties with those theoretically calculable. It is apparent from the dialogue which has emerged subsequent to proposals for establishing nmr ring current as a criterion of aromaticity[3c,d,13] that the physical properties used must be chosen to fit the compound in question and that the appropriate model compounds must be available for theoretical and experimental comparison.

The experimentally determined dipole moment is one of the most direct quantitative measures of charge separation on the ground state of a molecule. Correlations of the dipole moment and the theoretically calculated electron distribution provide a means of assessing

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(1) A preliminary report of this work appeared in *Tetrahedron Lett.*, 4467 (1967).

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(3) (a) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960); (b) H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity, *J. Am. Chem. Soc.*, **90**, 811 (1968); (c) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961); (d) R. Breslow, J. Brown, and J. J. Gajewski, *J. Am. Chem. Soc.*, **89**, 4383 (1967); (e) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *ibid.*, **84**, 4307 (1962); (f) E. Evleth, J. Berson, and S. Manatt, *Tetrahedron Lett.*, 3087 (1964).

(4) (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 279; (b) T. Nozoe in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, New York, N. Y., 1959, Chapter VII; (c) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, p 383; (d) D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier Publishing Co., Amsterdam, The Netherlands, 1966, Chapter VI; (e) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, London, 1969, p 85.

(5) (a) H. J. Dauben and H. J. Ringold, *J. Am. Chem. Soc.*, 73, 876 (1951); (b) W. von E. Doering and F. L. Detert, *ibid.*, 73, 876 (1951).

(6) C. D. Gutsche, "The Chemistry of Carbonyl Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1967, p 8.

(7) (a) G. M. Pilling and F. Sondheimer, *J. Am. Chem. Soc.*, **90**, 5610 (1968); (b) G. R. Proctor and A. H. Renfrew, *Chem. Commun.*, 696 (1966); (c) M. J. Cook and E. J. Forbes, *Tetrahedron*, 24, 4501 (1968); (d) W. Baker and J. McOmie in "Progress in Organic Chemistry," Vol. 3, J. W. Cook, Ed., Butterworth and Co., Ltd., London, 1955, p 64; (e) H. L. Ammon, P. H. Watts, Jr., J. M. Stewart, and W. L. Mock. *J. Am. Chem. Soc.*, **90**, 4501 (1968); (f) R. Breslow, *Chem. Eng. News*, 91 (June 28, 1965); (g) H. Hosoya, J. Tanaka, and S. Nagakura, *Tetrahedron*, **18**, 859 (1962).

(8) R. B. Turner in "Theoretical Organic Chemistry, The Kekulé Symposium," Butterworth and Co., Ltd., London, 1959, p 69.

(9) K. Kimura, S. Sazuki, M. Kimura, and M. Kubo, *J. Chem. Phys.*, 27, 320 (1957); *Bull. Chem. Soc. Japan*, **31**, 1051 (1958).

(10) (a) D. P. Craig in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, New York, N. Y., 1959, p 29; (b) T. Nozoe, T. Mukai, K. Takase, and T. Nagase, *Proc. Japan Acad.*, **28**, 477 (1952).

(11) (a) A. Di Giacomo and C. P. Smyth, *J. Am. Chem. Soc.*, 74, 4411 (1952); (b) Y. Kurita, S. Seto, T. Nozoe, and M. Kubo, *Bull. Chem. Soc. Japan*, 26, 272 (1953).

(12) E. D. Bergman in ref 7d, Chapter 3.

(13) (a) R. J. Abraham, R. C. Sheppard, W. A. Thomas, and S. Turner, *Chem. Commun.*, 43 (1965); (b) J. A. Elvidge, *ibid.*, 160 (1965); (c) W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Am. Chem. Soc.*, **89**, 1438 (1967); (d) J. I. Musher, *J. Chem. Phys.*, **43**, 4081 (1965).

π-electron delocalization,[3f] which is predicted to be dependent upon charge separation for molecules such as tropone.

One of the problems inherent in this approach is illustrated by the unduly large significance given to the dipole moment of tropone (4.30 D).[4,6,7,11,12] Although tropone exhibits a larger dipole moment than cycloheptanone or benzaldehyde, it cannot be assumed to possess an exceptional amount of dipolar or aromatic character on this basis. The best model compound for comparative purposes would be a completely localized cycloheptatrienone structure in which the double bonds do not interact with each other. Since this hypothetical molecule is unavailable and theoretically impossible by the precepts of quantum mechanics, difficulties arise which are similar to those encountered in choosing the proper models for the calculation of the resonance energy of benzene.[14] In the case of tropone, the dipole moments of cyclic unsaturated ketones, which approximate the cycloheptatrienone structure, would be of interest. The dipole moments of the compounds listed in Table I have been studied accordingly. A correlation of experimental dipole moments with those calculated from a satisfactory quantum mechanical theory should provide the necessary background for evaluating the electronic structure of tropone. Thus, the calculated electron densities and π-bond orders for a series of compounds can be examined for deviations indicative of extra π-electron delocalization. Also, any changes in the input geometry which might be necessary to provide a satisfactory calculated dipole moment for tropone may indicate the degree to which tropone differs from a nonaromatic polyunsaturated ketone.

Molecular orbital calculations utilizing the π-electron approximation have been of great use in furthering the understanding of conjugated planar hydrocarbons. The paucity of knowledge concerning σ-electron distributions and their interaction with the π system would, however, present a serious problem if these calculations were performed on the unsaturated ketones in Table I. A self-consistent method which includes all of the valence shell electrons and explicitly treats the charge separation inherent in the carbonyl group is therefore desired. The complete neglect of differential overlap or CNDO/2 theory developed by Pople, Santry, and Segal[15] fulfills these criteria and further requires only the molecular geometry of the molecule in question for input data, thus making it possible to account for conformational differences. The problem of calculating dipole moments from the π-electron densities and then including standard bond moments for the σ framework is obviated since the interaction of the σ- and π-electron systems is treated explicitly. From Pople and Gordon's calculations[16] and those presented in this work it is apparent that the CNDO/2 theory calculates dipole moments for ketones and aldehydes in good agreement with experiment.

Table I provides a summary of the relevant total electron densities, the π components of the electron densities, π-bond orders, and dipole moments of several ketones and aldehydes calculated by the CNDO/2 method. These calculations were based on the set of standard bond lengths and bond angles proposed by Pople and Gordon[16] unless otherwise noted. These standard values are in reasonable agreement with the available molecular parameters determined by electron diffraction or X-ray crystallography. Before considering tropone, a discussion of the trends in the charge distribution of unsaturated ketones and aldehydes is desired. The acyclic systems, some of which have been studied previously,[16] will be considered first.

From their analysis of formaldehyde, acetaldehyde, and acetone, Pople and Gordon[16] found that the dipole moment increases in this series primarily as result of an increasing polarization of the π electrons in the carbonyl group. The hyperconjugative transfer of electron density from the methyl group into the p_z orbital on oxygen is a general aspect of the CNDO/2 theory, and an analogous mechanism appears to operate whenever an alkyl group is substituted on a double bond.

It is difficult to discuss charge distribution within the σ framework of these molecules according to classical hybridized descriptions of atomic orbitals. This does not represent a theoretical problem since the CNDO/2 theory was designed specifically[15a] so that the electronic structural results of a calculation would be invariant with respect to an orthogonal transformation within the basis set of atomic orbitals. Thus, although the orbitals on carbon are not couched in the form of trigonal and tetrahedral hybridization, they are linearly combined in a manner which gives the same total charge distribution, and for planar conjugated systems, the same π-charge distribution as would hybridized orbitals.

An example of how this treatment leads to results differing from normal expectations regarding the σ framework is provided by the p_y orbitals in formaldehyde. The two electrons on oxygen usually considered to be nonbonding are partially "back-donated" through the carbon p_y orbital onto a hydrogen group orbital. This may perhaps be interpreted as a compensation for the oppositely directed charge distribution in the π orbitals. Thus the σ system works reciprocally with the π system, and neither one distributes its electrons independently of the other.

The CNDO/2 theory predicts that the charge separations across the carbonyl groups of acrolein and acetaldehyde should be essentially equal. Acetaldehyde, however, exhibits a slightly greater theoretical π-charge separation across the CO bond than does acrolein. This difference in π-charge distributions results from the tendency of an alkyl group to redistribute the π electrons in an adjacent double bond. The calculations on acrolein show a net drift of π-electron density from the β carbon onto oxygen. This is in accord with the predictions of resonance theory.

Crotonaldehyde has a larger theoretical dipole moment than does acrolein in concurrence with the experimental values. The methyl group of crotonaldehyde exerts a very small perturbation on the carbonyl

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(14) Reference 4a, Chapter 9.

(15) (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 43, S129 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, 43, S136 (1965); (c) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966). The program written by G. A. Segal was obtained through the Quantum Chemistry Program Exchange at Indiana University.

(16) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967). The standard bond angles used were 120 and 109.47° and the bond lengths in ångströms were $C_3{=}C_3$, 1.34; $C_3{-}C_4$, 1.52; $C_4{-}C_4$, 1.54; $C_3{=}O$, 1.22; $C_3{-}O_2$, 1.36; $C_4{-}O_2$, 1.43; $C_4{-}H$, 1.09; $C_3{-}H$, 1.08, where the subscript refers to the number of adjacent atoms to which the atom in question is bonded.

Table I. The Results of CNDO/2 Calculations for Several Aldehydes and Ketones[m]

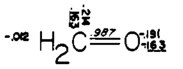
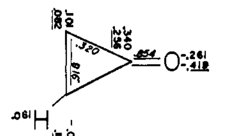
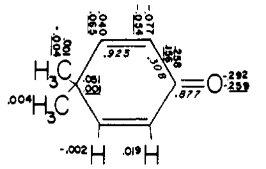
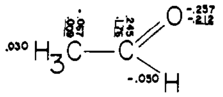
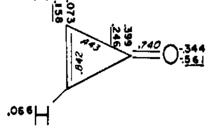
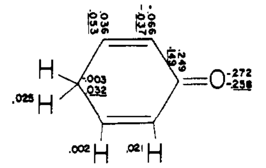
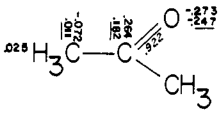
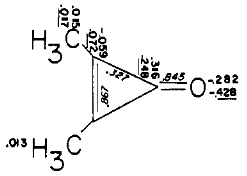
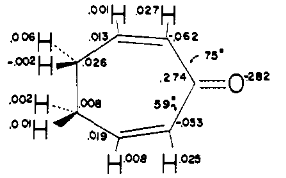
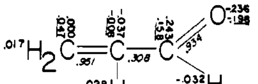
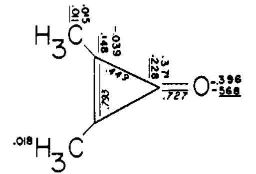
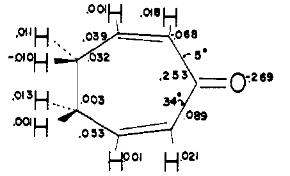
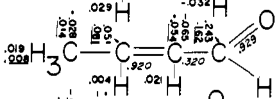
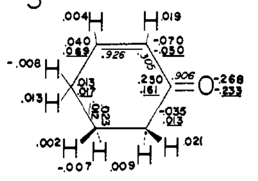
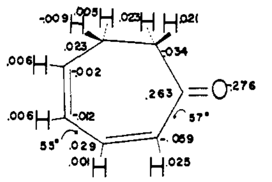
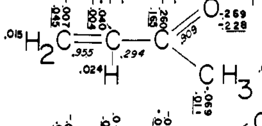
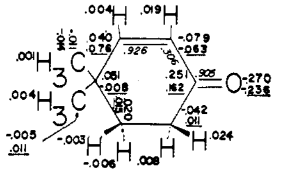
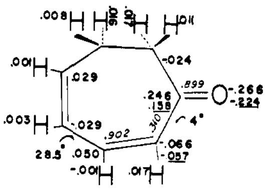
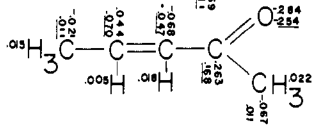
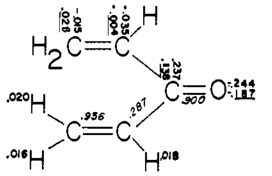
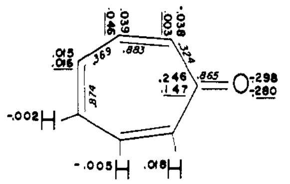
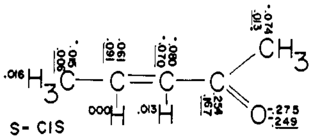
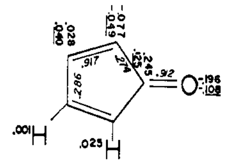
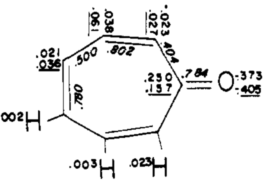
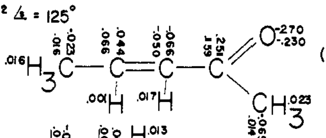
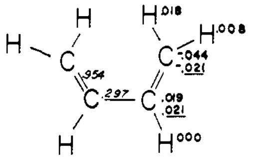
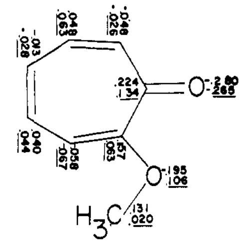
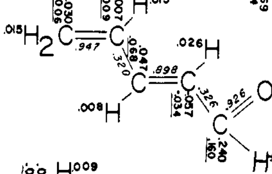
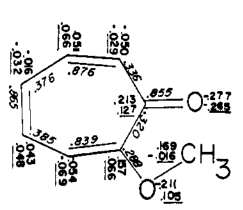
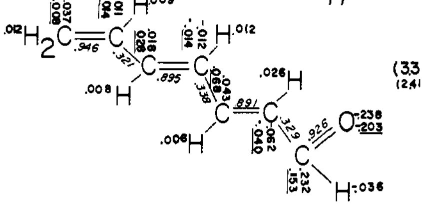
	μ		μ		μ
	2.34^{a} (2.00) (1.06)		(3.48) (1.50)		4.35^{j} (4.46) (5.09)
	2.68^{b} (2.53) (1.48)		$(5.09)^{h}$ (2.74)		(4.07) (2.60)
	2.90^{c} (2.95) (1.79)		$(3.73)^{i}$ (2.03)		4.04^{j} (3.21) (1.98)
	3.11^{d} (2.66) (1.62)		$(5.49)^{h}$ (3.34)		(3.70) (2.54)
	3.50^{e} (3.24) (2.12)		3.62^{j} (3.40) (2.15)		3.30^{j} (2.94) (1.84)
	3.16^{f} (2.98) (1.85)		3.66^{j} (3.59) (2.44)		(3.25) (2.06)
	3.26^{g} (3.53) (2.32)		(2.65) (1.77)		4.30^{j} (3.88) (2.47)
 S- CIS	(2.37) (1.14)		(2.37) (1.24)		$(5.49)^{k}$ (3.58)
sp² ∠ = 125° 	(3.37) (2.23)				4.72^{j} (4.76) (2.41)
	(3.11) (2.10)		4.72 (3.30) (1.60)		
	(3.39) (2.41)				

Table I *(Footnote)*

[a] J. N. Shoolery and A. H. Sharbaugh, *Phys. Rev.*, **82**, 95 (1951). [b] R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *J. Chem. Phys.*, **31**, 882 (1959). [c] J. D. Swalen and C. C. Costain, *ibid.*, **31**, 1562 (1959). [d] R. J. Wagner, J. Fine, J. W. Simmons, and J. H. Goldstein, *ibid.*, **26**, 634 (1957). [e] J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949); see also ref 9. [f] P. D. Foster, V. M. Rao, and R. F. Curl, Jr., *J. Chem. Phys.*, **43**, 1064 (1965). [g] G. K. Estok and J. S. Dehn, *J. Am. Chem. Soc.*, **77**, 4769 (1955). [h] Calculated from the bond lengths of tetrachlorotriafulvalene; quoted in H. Hosoya and S. Nagakura *Theor. Chim. Acta* (Berlin), **8**, 319 (1967). The bond lengths used were 1.31 Å for C=C and 1.39 Å for C—C. [i] For comparative purposes the dipole moment of di-*n*-propylcyclopropenone is 4.78 D: R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1326 (1965). [j] This work. [k] Calculated for a regular heptagonal geometry, C—C bond lengths equaling 1.41 Å. [l] Y. Kurita, S. Seto, T. Nozoe, and M. Kubo, *Bull. Chem. Soc. Japan*, **26**, 272 (1953). [m] The numbers next to a given atom are the calculated electron densities; the upper value is the total electron density and the lower value (underlined) is the π-electron density. The italicized number printed along a bond is the π-bond order. The dipole moments not enclosed in parentheses are experimental values. The total theoretical dipole moment is the value in larger print enclosed in parentheses, and the component of the calculated dipole moment which arises from the electron densities is the value in smaller print enclosed in parentheses.

polarization. It does, however, redistribute the electrons on the vinyl group causing the β vinyl carbon to become positive in contrast to the over-all zero charge predicted for the β vinyl carbon of acrolein. A comparison of formaldehyde, acetaldehyde, acrolein, and methyl vinyl ketone indicates that the effects of a methyl and vinyl group on the dipole moment and carbonyl polarization are essentially additive. The predicted dipole moment of 3-penten-2-one is higher than the experimental value. However, it has been suggested that the experimental value is low because at equilibrium this ketone contains an appreciable population of the *s-cis* rotamer.[17]

Considering the data of Table I, it can be seen that generally the theoretical values are slightly low but the agreement is in fact quite good. Considering the residual errors that do occur, the higher and more nearly correct values arise from the more highly alkylated compounds. Therefore it appears that this theory underestimates the π-polarization contribution of the carbonyl in predicting dipole moments.[18] By overestimating the electron displacement effect of a saturated carbon atom at the terminus of multiple bonds, the theory yields an agreement between experimental and predicted values which becomes deceptively better as the ratio of saturated to unsaturated carbon atoms increases.

Calculations on pentadienal illustrate the effects caused by extended conjugation. The π-bond orders across the formal single and double bonds tend to converge more for pentadienal than acrolein. Correspondingly, the polarization of the carbonyl group and the adjacent double bond are larger for pentadienal than for acrolein, but by a rather small amount. The effect of the carbonyl group on the terminal double bond of pentadienal is very small as indicated by the reversal of electron densities, which now closely resemble those calculated for butadiene. Within the π framework, however, some electron density has been drawn from this terminal double bond toward the carbonyl group.

For our model of pentadienone, the bond angles were opened to 128° to alleviate the steric interaction of the two inner terminal hydrogens. However increasing these bond angles can be shown to lower the theoretical carbonyl group polarization (see below) and 1,4-pentadien-3-one cannot be strictly compared with acrolein and pentadienal for this reason.

Because of the conformational uncertainty in acyclic compounds which results from rotation about formal single bonds it is desirable to extend this analysis to cyclic conjugated ketones. From Dreiding models it is apparent that the double bonds of cyclohex-2-enone and cyclohexa-2,5-dienone are coplanar with the carbonyl groups. The calculated charge distributions in cyclohex-2-enone and 3-penten-2-one may be compared. The vinyl groups have almost identical charge distributions and π bond orders, but the carbonyl group of cyclohex-2-enone is less polarized than that of 3-penten-2-one as a result of a redistribution of charge in the aliphatic portion of cyclohex-2-enone. When cyclohex-2-enone is substituted with two methyl groups at the 4 position, the theoretical dipole moment increases by 0.2 D while the experimental dipole moment remains the same. This same effect, though of twice the magnitude, is seen upon substituting two methyl groups in the 4 position of cyclohexa-2,5-dienone. Further evidence is thus provided that the CNDO/2 theory overemphasizes the hyperconjugative effects of methyl substitution. Although the calculated dipole moment of 4,4-dimethylcyclohex-2-enone is in closer agreement with experiment than is the calculated moment of cyclohex-2-enone, the lower value for cyclohex-2-enone is in better agreement with the trends already observed.

The theoretical dipole moment increases by 0.71 D from cyclohex-2-enone to cyclohexa-2,5-dienone, but the polarization of the carbonyl groups of these compounds is predicted to be about the same. The predicted increase in dipole moment arises from the charge separation across the additional double bond. Comparing 4,4-dimethylcyclohex-2-enone and 4,4-dimethylcyclohexa-2,5-dienone, however, the polarization of the carbonyl group is predicted to increase with addition of the second double bond. This effect is due primarily to the prediction that the methyl groups of 4,4-dimethylcyclohexa-2,5-dienone contribute more electron density to this system through orbital overlap than do hydrogens in the 4 position.

As a result of our desire to study models which approximate the structure of tropone, we have measured the dipole moments of cyclohepta-2,4-dienone and cyclohepta-2,6-dienone.[19] Unfortunately there is considerable conformational and configurational uncertainty about these molecules. Evidence from the nmr spectra of these compounds suggests that the internal angles resemble those for tropone.[20]

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(17) G. K. Estok and J. S. Dehn, *J. Am. Chem. Soc.*, 77, 4769 (1955).

(18) It should be noted that since the theoretical dipole moments are generally low, they could be brought into even better agreement by utilizing a slightly longer C=O bond length in the CNDO calculations.

(19) The coordinate systems for molecules which have nonzero *Z* components for carbon atoms were determined by using the ABC Kapra computer program originally written by Tolles.

A preliminary calculation was performed on cyclohepta-2,6-dienone utilizing the standard bond angles of 120 and 109.47°. This geometry necessitated the use of the large values, 75 and 59°, for the dihedral angles H–C_7–C_1–O and H–C_2–C_1–O. However, the theoretically calculated dipole moment of 3.21 D based on this geometry indicates that this was an unrealistic model. Because experimental values are unavailable, the bond angles centered on the vinyl and carbonyl carbon atoms were arbitrarily opened to 125°, giving 5 and 34°, respectively, for H–C_7–C_1–O and H–C_2–C_1–O dihedral angles. The calculated dipole moment of 3.70 D based on this later model is 0.34 D lower than the experimental value and thus in reasonable agreement with the trend in calculated values. When the bond angles are opened to 125°, the polarization of the carbonyl group is lowered and the polarization of vinyl group is raised. In order to determine whether this effect was produced by increasing the bond angles or by making the conjugated system more coplanar, a calculation on 3-penten-2-one with 125° bond angles was performed. The polarization across the carbonyl decreased from this modification but the polarization of the vinyl group remained the same. Therefore for cyclohepta-2,6-dienone, the decrease in carbonyl polarization observed in the second model can be attributed to opening the bond angles (the decrease is the same in 3-penten-2-one) and the increase in vinyl polarization to the more planar π system.

A model for cyclohepta-2,4-dienone can be constructed geometrically using standard bond angles. This model exhibits dihedral angles for H–C_2–C_1–O and H–C_3–C_4–H of 53 and 57°, respectively. Because these angles are inconsistent with conformational evidence provided by nmr coupling constants,[20,21] a second model was constructed using 126.5° internal angles. The H–C_2–C_1–O and H–C_3–C_4–H dihedral angles of 4 and 28.5° for this model are more consistent with the nmr data for this compound.

Two models were chosen for the CNDO calculations on tropone, the first, a regular heptagon utilizing the available electron diffraction data,[9] the second, a planar model built from standard alternating bond lengths and internal angles of 128 ± 0.5°. These standard bond lengths used in the second model appear quite reasonable since the recommended C=C bond length is identical with that observed in 2-chlorotropone[22] and the C–C bond lengths do not differ significantly from those of the C_5–C_6 and C_7–C_1 bonds of 2-chlorotropone. As will be shown shortly the second model conforms more accurately to reality.

The result of the CNDO/2 theory using this second model can be compared to the other molecular orbital calculations which have been performed on tropone. Brown[23] did the first Hückel molecular orbital (HMO) calculations on tropone in 1951, the same year that it was first synthesized. He concluded from his treatment that a charge-separated tropylium oxide appeared to provide a faithful picture of the general electronic structure of tropone. It is now apparent that HMO theory does a reasonable job with alternate planar aromatic hydrocarbons, but when it is applied to molecules which contain heteroatoms, possess odd-membered rings, or have uneven charge distributions the theory is often wholly inadequate and may lead to many false assumptions. An excellent discussion of these problems is provided by Dewar.[24] Tropone possesses all of the above-mentioned drawbacks. However, HMO theory has been used recently as a comparative tool for assessing the relative *aromaticity* of tropone, benzotropone, and the newly synthesized furotropone.[25]

Of the SCF π-electron calculations which have been performed on tropone, Julg and Bonnett's[26] agree best with the results predicted by CNDO/2 theory. This is not surprising since the bond lengths predicted by Julg and Bonnett are within 0.01 Å of the standard bond lengths used in our calculations. The dipole moment of 5.6 D which they predict is too high, and their calculations predict a greater shift of electron density from the ring onto the carbonyl oxygen than does the CNDO theory. Inuzuka and Yokota[27] used the electron diffraction bond lengths and calculate a much higher electron density on the carbonyl oxygen and a lower π-bond order across the carbonyl group than we do. Obtaining self-consistency for the bond lengths, Kuroda and Kunii[28] predict a dipole moment of 4.68 D, and although the carbon–carbon lengths alternate, the CO bond length of 1.27 Å may have led to the high predicted electron density on the carbonyl oxygen that these authors calculated.

The electron diffraction patterns obtained for tropone were fitted assuming all of the carbon–carbon bonds to be equal in length. It was pointed out by the authors of the original work[9] that the data could be fitted equally as well using a model employing bond alternation. A regular heptagonal structure, however, is completely inconsistent with the nmr coupling constants[20] for tropone, the X-ray crystallography[22] work on 2-chlorotropone, and the dipole moment.

The CNDO/2 calculations utilizing standard bond lengths yield a dipole moment of 3.88 D for tropone. Compared to the experimental value of 4.30 D, this value is characteristically low, in fact by almost the same amount as the theoretical value for acrolein. Using a regular heptagonal geometry, the theory calculates a moment of 5.49 D, which is more than 1.0 D too high and indicates an erroneous geometrical assignment.

From these observations it is reasonable to state, although no direct accurate measurements are available, that tropone has bond lengths within the range found for normal polyolefinic compounds. Even though the double and single bonds are localized, it is still possible to ask whether the charge separation and dipole moment are typical for a conjugated ketone. In comparison with cycloheptanone or benzaldehyde, tropone certainly has a high dipole moment, but, in comparison with better model compounds, such as 4,4-dimethyl-

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[20] D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *J. Am. Chem. Soc.*, **91**, 5286 (1969).

[21] A. A. Bothner-By and E. Moser, *ibid.*, **90**, 2347 (1968).

[22] E. J. Forbes, M. J. Gregory, T. A. Hamar, and D. J. Watkin, *Chem. Commun.*, 114 (1966).

[23] R. D. Brown, *J. Chem. Soc.*, 2671 (1951). This conclusion was a reasonable interpretation due to the lack of experimental data then available.

[24] M. J. S. Dewar in "Aromaticity," The Chemical Society, Special Publication No. 21, Burlington House, London, 1967.

[25] D. R. Burnham and M. J. Cook, *Tetrahedron Lett.*, 3771 (1968)

[26] A. Julg and M. Bonnett, *Tetrahedron*, **20**, 2243 (1964).

[27] K. Inuzuka and T. Yokota, *J. Chem. Phys.*, **44**, 911 (1966).

[28] H. Kuroda and T. Kunii, *Theor. Chim. Acta* (Berlin), 7, 220 (1967).

cyclohexa-2,5-dienone or cyclohepta-2,6-dienone, it is quite normal. Examination of the predicted charge densities of tropone and acrolein indicates that the theory does predict the oxygen atom of tropone to be more negative, while the charges on the carbonyl carbons are essentially the same. This greater polarization is derived from electron migration out of the ring in tropone onto the oxygen atom; but the amount of extra electron release per carbon atom is relatively small. Comparison of the predicted charge densities and π polarization of tropone with those of the cycloheptadienones or cyclohexadienones leads to a smaller discrepancy. The theoretical π-bond orders of the formal double bonds of tropone are slightly lower than those of the remaining acyclic six- and seven-membered ring systems considered in Table I. However, the formal single C_1–C_2 π-bond order predicted for tropone is essentially identical with that predicted for the C_1–C_2 bond of heptatrienal. Thus the lower predicted π-bond orders for the formal double bonds of tropone appear to derive from increased conjugation within the carbon framework rather than increased polarization. Taken as a whole, the data of Table I can be interpreted to indicate that tropone does deviate slightly from the remaining acyclic, six- and seven-membered ring ketones considered in this study, but the magnitude of this deviation is clearly not consistent with realization of the cyclic π-electron delocalization anticipated by resonance structure **1b**. The more important remaining data often cited to assign aromatic character to tropone are diamagnetic susceptibility, empirical resonance energy, basicity, and infrared carbonyl stretching frequency.[29–31] The experimental diamagnetic susceptibility of tropone ($54 \times -10^6\chi$) when compared to the calculated value from Pascal's constants ($41.2 \times -10^6\chi$) leaves a discrepancy of $12.8 \times -10^6\chi$.[10a] However, calculation of the diamagnetic susceptibility from more recent and more reliable data[32] leads to a value of $47.4 \times -10^6\chi$, leaving a discrepancy of $6.6 \times -10^6\chi$ (less than that for cycloheptatriene), which is of questionable significance.[3b] The experimental stabilization energy of tropone (11.9 kcal) is only 3 kcal greater than that of cycloheptatriene (9.0 kcal)[8] which is also inconsistent with assigning any significant aromatic character to tropone. Finally, the relatively high basicity of tropone can be attributed to the unusual stability of the conjugate acid[33,34] and does not necessarily reflect ground-state stabilization.

The planarity of tropone is consistent with available evidence since the π-stabilization energy exceeds the strain energy which can be estimated to be 7 kcal[35] by analogy with heptafulvene. Thus, tropone exhibits a sufficiently large π-stabilization energy to be planar, but the source of this stabilization is primarily that anticipated for a polyenone. The data also indicate that the cycloheptadienones are more nearly planar than would be anticipated from Drieding molecular models, suggesting that these systems possess π-stabilization energies but that they are less than the respective strain energies for fully planar systems. For these reasons it appears that tropone more closely resembles a polyenone than an aromatic system and would best be classified as the former.

With reference to chemical reactivity tropolones are generally considered to exhibit a greater degree of aromatic character than tropone.[4d] Since the dipole moment of tropolone 2-methyl ether is known,[11b] CNDO/2 calculations were performed on this molecule using the standard bond lengths. As can be seen from the data of Table I, the predicted dipole moment is highly dependent on the orientation of the methoxy group as would be expected. The agreement between the experimental and the theoretical dipole moment for the *anti*-methoxy rotamer is excellent. The somewhat better agreement observed between the experimental and theoretical values in this case in contrast to most of the data of Table I may be due to the fact that the *syn*-methoxy rotamer is present to some extent and therefore the experimental value is not that of the pure *anti*-methoxy rotamer. In any case the agreement is quite satisfactory and tropolone 2-methyl ether closely correlates with the remaining polyenones studied in this work. Therefore, the dipole moment of tropolone 2-methyl ether indicates that this molecule does not exhibit any greater amount of aromatic character than tropone and is also adequately described as a polyenone.

With respect to the previous discussion it is now interesting to consider cyclopropenone. From the CNDO/2 calculations on cyclopropenone, it is apparent that the bond lengths used are highly critical in determining the predicted charge densities.[36–38] However, regardless of the model used, the theory does predict a larger π polarization for this system than the remaining compounds considered in Table I. This result, which is in agreement with other recently reported SCF–MO calculations on cyclopropenone,[39] might have been anticipated intuitively since the electrostatic work necessary to achieve a cyclopropenium oxide structure would be considerably less than that necessary for the cycloheptatrienylium oxide structure. For this reason, cyclopropenone is expected to be a closer approximation to an aromatic system among the possible cross-conjugated compounds which rely on dipolar resonance structures to form cyclic delocalized π systems.[31]

Finally, turning to cyclopentadienone the CNDO/2 calculations predict that this molecule should exhibit

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(29) The carbonyl stretching frequency in the infrared spectrum is often quoted as a measure of the dipolar character of tropone.[6,14a,30] The recent work of Krebs and Schrader[31] has established that the 1590-cm^{-1} band is due to the CO stretch in tropone. However, the significance of the low frequency of the CO bond in tropone with respect to the ground state of the molecule is rather obscure, especially in light of the observed strong coupling of the CO and C═C bonds.

(30) (a) Reference 12b, p 142; (b) V. Zaitsev, Y. Sheinker, Y. Kareshkov, and M. E. Vol'pin, *Chem. Abstr.*, **59**, 12303 (1963); (c) Y. Ikegami, *Bull. Chem. Soc. Japan*, **34**, 972 (1962).

(31) A. Krebs and B. Schrader, *Liebigs Ann. Chem.*, **709**, 46 (1967).

(32) W. Haberdtizl, "Über Ein Neues Diamagnetismus-Inkrementsystem," "Stizungsberichte der Deutschen Akademie der Wissenschaften zu Berlin," Akademie-Verlag, Berlin, 1964.

(33) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, p 355–367.

(34) William Mullin, M. S. Thesis, University of California at Santa Barbara, 1967.

(35) Reference 4a, p 244.

(36) Although the bond lengths suggested by Pople and Gordon would be expected to be generally applicable, they might not be satisfactory for highly strained systems such as cyclopropenone. For this reason calculations employing both the standard bond lengths and those derived from the crystal structure of the three-membered ring of tetrachlorotriafulvalene[37] were performed. The experimental dipole moment for di-*n*-propylcyclopropenone (4.78 D)[38] is comparable to the calculated values.

(37) See Table I, footnote *h*.

(38) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1326 (1965).

(39) A. Watanabe, H. Yamaguchi, Y. Amako, and H. Azumi, *Bull. Chem. Soc. Japan*, **41**, 2196 (1968).

the lowest charge density on the oxygen of the compounds considered in Table I. Thus, the CNDO/2 theory does tend qualitatively to anticipate the $4n + 2$ rule in cross-conjugated systems by predicting slightly enhanced π polarization in tropone and cyclopropenone, and a low π polarization for cyclopentadienone, but attributes to this rule a considerably less significant position for these systems than organic chemists are accustomed to. There are numerous additional molecules for which it is possible to write dipolar resonance structures, which generate cyclic $4n + 2$ π systems. However, quite often aromatic character has been assigned to these compounds on the basis of dipole moments and other data without consideration of suitable reference compounds,[40] and therefore these assignments must be considered intuitive at best.

Experimental Section

The compounds studied in this work, 4,4-dimethylcyclohex-2-enone, 4,4-dimethylcyclohexa-2,5-dienone, cyclohepta-2,6-dienone,[41] cyclohex-2-enone,[42] cyclohepta-2,4-dienone,[43] and tropone,[44] were prepared by literature methods. These compounds were further purified by preparative gas chromatography on a 12-ft $^3/_8$-in. column of 16% DEGS on 60–80 mesh Chromosorb W operating at approximately 100° followed by evaporative distillation.

The dipole moments were obtained from dielectric constant measurements at 25° using a Dipolmeter DMO1 manufactured by Wissenshaftlich-Technische Werkstatten with the corresponding gold-plated DFL2 measuring cell which was thermostated to ±0.02°. The solvent used in the dipole moment determinations was Baker and Adamson reagent grade benzene which was further purified and dried by triple distillation through a Vigreux column from phosphorus pentoxide. The dipolmeter was calibrated before each determination by a least-squares plot of instrument reading *vs.* dielectric constant for cyclohexane, benzene, and toluene. The solution densities were determined with a 3-ml capacity Kontes pycnometer (K-329000). The electronic polarizabilities were determined with the aid of a Bausch and Lomb dipping refractomer, Type 33-45-26; and in all cases the atomic polarizability was set equal to 10% of the electronic polarizability. Dipole moment calculations were performed by a program written for an IBM 360/65 computer using the method of Halverstadt and Kumler.[45]

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[43] E. E. van Tamelen and G. T. Hildahl, *ibid.*, **78**, 4405 (1956).

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[45] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

The Synthesis and Study of Pseudoaromatic Compounds. X. A Reevaluation of the Question of Aromatic Character in Tropone, Tropolone, and Substituted Heptafulvenes Based on the Analysis of the Nuclear Magnetic Resonance Spectra of These and Several Related Compounds

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Abstract: Analyses of the nmr spectra of tropone, 2-chlorotropone, tropolone, tropolone 2-methyl ether, 5,6-benzotropolone, 1,3-dideuterioazulene, 2-indenyltropenium ion, the conjugate acid of tropone, methoxytropenium ion, 8,8-dicyanoheptafulvene, 3,3-dimethyl-2-cycloheptatrienylideneindanone, cyclohepta-2,4-dienone, 2-methylstyrene, 6-dichloromethyl-6-methylcyclohexa-2,4-dienone, and the conjugate acid of 6-dichloromethyl-6-methylcyclohexa-2,4-dienone are reported. Correlation of the coupling constants of these compounds and those of several related systems indicates that tropone, tropolone, and 8,8-dicyanoheptafulvene exhibit bond alternation characteristic of polyenones and polyenes, and thus do not exhibit appreciable aromatic character.

In a previous paper we presented evidence that the dipolar character of tropone has been greatly overestimated and that tropone exhibits properties closely resembling those of a polyenone.[2] In the present paper we extend our study of tropone and some related systems through analyses of their nmr spectra.

There is a paucity of nmr coupling constant data for fully unsaturated seven-membered ring compounds, primarily as a result of the complexity of the nmr spectra that these systems exhibit. The nmr spectra of tropone, for instance, has been reported to be a broad singlet in carbon tetrachloride.[3] Coupling constant data for

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