

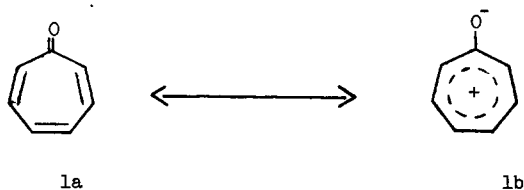
AN ANALYSIS OF THE DIPOLE MOMENTS OF SIX- AND SEVEN-MEMBERED
RING CYCLIC UNSATURATED KETONES

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Although the subject of the importance of dipolar resonance contributor lb to the ground state of tropone has been extensively discussed,⁽¹⁾ sufficient data has not been available to



fully resolve this point. Even though it is clear that tropone is not aromatic, resonance structure lb has been assumed to make a significant contribution to the ground state⁽¹⁾ of this molecule. This assumption is based primarily upon comparison of the dipole-moments of tropone with simple ketones such as cycloheptanone.⁽²⁾

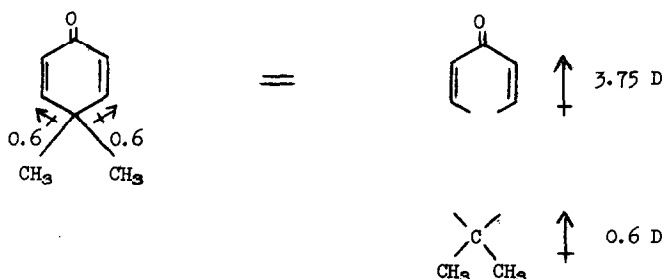
In an attempt to gain a better perspective on this point, we have measured the dipole moments of the compounds in Table 1.⁽³⁾ Although dipole moment data should be an excellent criteria for establishing the importance of dipolar resonance contributors,⁽⁵⁾ often suitable model compounds are not available for a sound analysis. However, we feel the compounds studied in this work represent a satisfactory set of model compounds upon which to base a reasonable conclusion. In order to evaluate the contribution from lb to tropone it is necessary to estimate the expected dipole moment based on a polyenone model and compare this value to the experimental number. In principle it should be possible to analyze the dipole moments of compounds listed in Table 1 by dissecting out the π -components from the sigma components.⁽⁶⁾ Such an analysis is difficult since there is no uniformly accepted set of bond dipoles. However, a qualitative, yet worthwhile, analysis is possible which minimizes the use of empirical bond moments.

TABLE 1

Compound	$\mu \pm .05, D.$ This work*	$\mu, D.$ Lit. ⁴
cyclohexanone	3.08	3.09
cyclohex-2-enone	3.62	
4,4-dimethylcyclohexanone (2)	3.09	
4,4-dimethylcyclohex-2-enone (3)	3.66	
4,4-dimethylcyclohexa-2,5-dienone(4)	4.35	
cycloheptanone (5)	3.03	
cyclohept-2-enone (6)	3.45	
cyclohepta-2,6-dienone (7)	4.04	
tropone (1)	4.30	4.17, 4.30

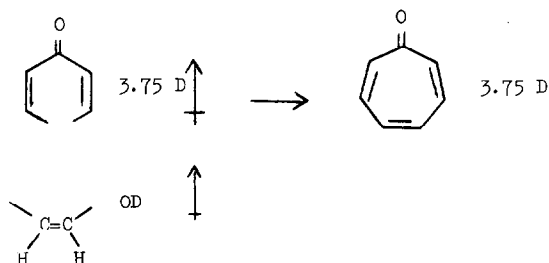
* All of the dipole moments were obtained from dielectric constant measurements in benzene solution at 25° using a Dipolemeter DM01 manufactured by Wissenschaftlich-Technische Werkstätten with the corresponding gold plated DFL2 measuring cell. The dipole moments were calculated with a computer program using the Halverstadt-Kumler equation. The electronic polarizabilities were determined with the aid of a Bausch and Lomb Dipping Refractometer Type 33-45-26; and in all cases the atomic polarizability was set equal to 10% of the electronic polarizability.

A Dreiding molecular model of 4,4-dimethylcyclohexa-2,5-dienone (4) indicates that the π -system of this molecule can be planar without introducing any significant strain.⁽⁷⁾ It is possible to dissect the dipole moment of this molecule into two fragments, the first arising from the π -system comprised of carbon atoms 1,2,3,5 and 6 and the second from the sigma moment derived from carbon 4. The component derived from carbon 4 arises from the sp^2 - sp^3 carbon-



carbon bond moment of an alkyl group at the β -position of an α,β -unsaturated carbonyl system, and has been estimated to be 0.6 D along the bond.⁽⁸⁾ The resulting π -system dipole moment, which should be characteristic of a planar $\alpha,\beta,\alpha',\beta'$ -unsaturated ketone, is then estimated to be 3.75 D.

To a first approximation, it should be possible to construct a planar model for tropone by fusion of the above calculated $\alpha,\beta,\alpha',\beta'$ -unsaturated ketone system to an ethylene unit. Since



in this process only sp^2 - sp^2 carbon-carbon bonds are formed, there would be no net expected increase in the sigma contribution to the dipole moment. However, the fact that the length of the conjugated system has increased, should increase the π -dipole component. Since it is impossible to evaluate this latter factor, it is only possible to estimate a lower limit of the expected dipole moment of tropone (or upper limit from lb) based upon this model. This leaves a discrepancy of 0.55 D between the measured and calculated dipole moments of tropone.

Assuming that this discrepancy arises from the separation of point charges from the center of the seven-membered ring to the oxygen atom, and estimating this distance from the known structure of 2-chlorotropone,⁽⁹⁾ the charge separated is 0.19 esu. This leads to an estimated contribution from lb of ca. 4% in excess of that expected for a simple unsaturated ketone.⁽¹⁰⁾

It is worth noting that from heat of hydrogenation data⁽¹¹⁾ tropone is reported to exhibit a stabilization energy of only 2.9 Kcal. in excess of the nonplanar cycloheptatriene.⁽¹²⁾ However, the assumed planarity of tropone is consistent with a polyenone model. The nonplanarity of cycloheptatriene can be attributed to the strain energy associated with a sp^3 hybridized carbon atom in a seven-membered ring, which would be partially reduced by having all carbon atoms sp^2 hybridized. For example, the estimated strain energy of heptafulvene is

7 Kcal.⁽¹³⁾ which is less than the experimental stabilization energy (9 Kcal.) of cycloheptatriene.⁽¹¹⁾ Therefore, assuming that tropone possesses no greater strain energy than heptafulvene, the resonance energy associated with a polyenone model should be sufficient to overcome a strain energy of 7 Kcal.⁽¹⁴⁾

In order to verify the applicability of the above dipole moment analysis it is of value to consider the remaining data of Table 1. Turning to the series cycloheptanone (5), cyclohept-2-enone (6) and cyclohepta-2,6-dienone (7) it should be possible to calculate the observed dipole moments of 6 and 7 from the dipole moments of compounds 2-4. The smaller increase in the dipole moments within the series 5-7 can be accounted for by conformational considerations. The increase in dipole moment (0.57 D) in going from 4,4-dimethylcyclohexanone (2) to 4,4-dimethylcyclohex-2-enone (3) can be attributed to the effect of the additional conjugation. This same trend should be paralleled in going from cycloheptanone 5 to cyclohept-2-enone (6).

A Dreiding molecular model of cyclohept-2-enone (6) indicates that this molecule can assume three conformations, envelope, twist boat and boat. In the boat the π -system is planar, but the hydrogens on C₅ and C₈ are eclipsed and there is a severe cross ring interaction between the inner hydrogens of C₄ and C₇. Both the envelope and twist boat conformations appear to have approximately minimized steric interactions, and are assumed to be about equal in energy and more favorable than the boat conformation. An important aspect of the envelope and twist boat conformations is that the torsional angles between the carbonyl π -bond and the carbon-carbon π -bond are similar, $\sim 40^\circ$ for the twist boat and $\sim 50^\circ$ for the envelope. Assuming that the contribution to the dipole moment from the double bond should be proportional to the overlap across this torsional angle, this contribution from the carbon-carbon double bond should decrease as the cosine of the torsional angle. Using this assumption, the experimental dipole moment of cycloheptanone, the observed increase in going from 4,4-dimethylcyclohexanone to 4,4-dimethylcyclohex-2-enone (i.e., 0.57 D) and the torsional angle for the envelope or twist boat conformations of cyclohept-2-enone estimated from molecular models, allows calculation of the expected dipole moment for the envelope (3.39 D) and for the twist boat conformation (3.47 D) which are in reasonable agreement with that observed.⁽¹⁵⁾

Molecular models indicate that cyclohepta-2,6-dienone (7) has a single boat conformation. By a similar analysis based on torsional bond angles estimated from molecular models, and the increase in dipole moment in going from 4,4-dimethylcyclohexanone to 4,4-dimethylcyclohexa-2,5-dienone the dipole moment of cyclohepta-2,6-dienone can be calculated (3.90 D) which again is in reasonable agreement with the observed value.

A more detailed analysis of this and additional data including molecular orbital calculations will be presented later.

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14. The source of the stabilization energy of a polyene such as cycloheptatriene is not clear, and at this time it appears best to limit discussion to the above comparison.
15. It follows that using the same dipole moment data by approaching the problem from the opposite end, the torsional angle could be predicted. However, it is not possible to determine which conformation is more stable from this data.

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