

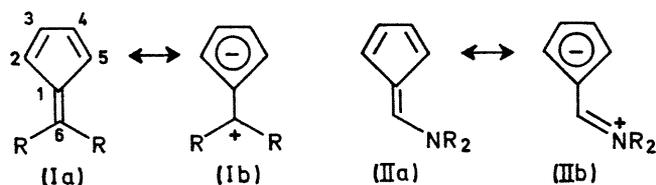
The Crystal Structure of 2-Formyl-6-dimethylaminopentafulvene. Bond Length and Angle Evidence for Dipolar Character

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Summary Bond lengths and angles found in a crystal structure study of 2-formyl-6-dimethylaminopentafulvene suggest that a dipolar form (IIIb) makes a major contribution to the ground-state resonance hybrid.

NUMEROUS experimental and recent theoretical studies have established that the simple pentafulvenes (I) are best represented as conjugated olefins (Ia) rather than as dipolar cyclopentadienides (Ib).¹ However, in cases such as the 6-dialkylaminopentafulvenes (II), molecules in which the



C(6) substituent is capable of substantial stabilization of the exocyclic positive charge, the dipolar forms (*e.g.*, IIb) are important for the description of the ground-state resonance hybrids. Studies of dipole moments, rotational barriers about the C(1)-C(6) and C(6)-N bonds and the five-membered-ring vicinal proton coupling constants² have provided evidence for enhanced charge separation and π -bond delocalization in the (II) series. We describe some preliminary work on the X-ray crystal structure of 2-formyl-6-dimethylaminopentafulvene (III), and present bond length and bond angle data which suggest that a dipolar form, best represented as (IIIb), makes a large contribution to the ground-state structure.

2-Formyl-6-dimethylaminopentafulvene³ crystallized from isopropyl alcohol-ligroin in the triclinic space group $P\bar{1}$ with cell dimensions of $a = 9.793 \pm 0.002$, $b = 11.971$

± 0.003 , $c = 7.608 \pm 0.002$ Å, $\alpha = 91.90 \pm 0.02$, $\beta = 110.03 \pm 0.02$, and $\gamma = 90.72 \pm 0.02^\circ$, and with $Z = 4$ (2 molecules per asymmetric unit). A 0.3 mm cubic specimen mounted in a thin-walled glass capillary was used for the X-ray intensity measurements. Three-dimensional data were collected on a computer-controlled Siemens AED diffractometer using Ni-filtered CuK radiation and the Siemens 5 point 2θ - θ scan technique. Of a total of 2362 reflections measured to a maximum 2θ of 120° , 1617 were three standard deviations above background and were

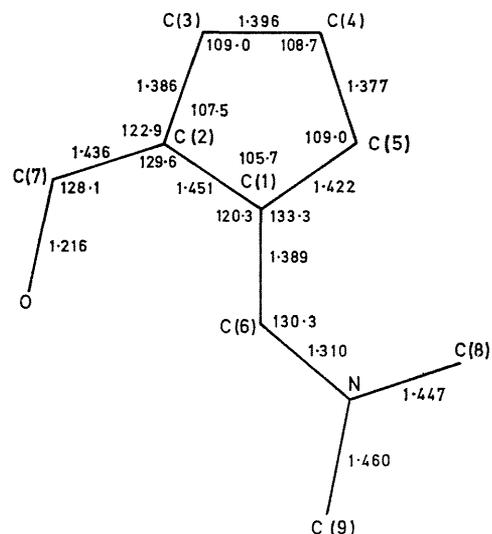
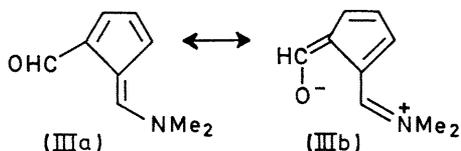


FIGURE. Average bond lengths (Å) and angles (degrees) for 2-formyl-6-dimethylaminopentafulvene. The mean difference between equivalent bonds in the two independent molecules is 0.004 Å. The maximum difference is 0.011 Å [N-C(9)]. The average standard deviation in bond lengths is 0.006 Å.



called "observed." The structure was solved using the symbolic addition method.⁴ Subsequent full-matrix least-squares refinement employing unit weights, individual anisotropic temperature factors for C, N, and O and isotropic terms for the H atoms gave a final R value of 0.046 for all observed data.†

† All calculations were done on the University of Maryland UNIVAC 1108 computer with the *Crystal Structure Program System*, ed. J. M. Stewart, Computer Science Center, University of Maryland.

The agreement between "equivalent" features in the two independent molecules is quite good, so that only the average structural parameters will be used in the following discussion. The molecular conformation is shown in the accompanying Figure. The C, N, O atoms are coplanar to a high degree with a mean atomic deviation of 0.017 Å from the 11 atom least-squares plane. Most of the bond distances (disregarding the 2 CH₃-N lengths) differ significantly from the usual values expected for the structure depicted as (IIIa), and all of the lengths point toward a major contribution from a canonical form such as (IIIb). Thus, considering the kinds of bonds shown in (IIIa), we find that the three C=C connections are long, the C(6)-N, C(1)-C(5), C(3)-C(4), and C(2)-C(7) single bonds are short, and C(1)-C(2) appears to be unaltered, all of which represent necessary changes for the (IIIa) → (IIIb) transition.

The 6.7° difference in the exocyclic bond angles at C(2) is probably a consequence of steric crowding between the formyl group and the C(1) substituent. A similar rationale, however, cannot be applied to the 13° difference in exocyclic angles at C(1), since the angular difference is one which increases, rather than decreases, the formyl-amino-methylene non-bonded interaction. There are numerous examples in the literature which show that the bond angles about a trigonal C atom (R¹R²C=X) are far from being equal, and that the smallest of the angles is almost invariably opposite the double bond (*i.e.*, ∠ R¹-C-R²). Therefore, if C(1)-C(5) does have substantial double-bond character then C(2)-C(1)-C(6) should be smaller than C(5)-C(1)-C(6), and this seeming discrepancy in the C(1) angles is, in actual fact,

additional evidence for the importance of (IIIb) to the ground-state resonance hybrid.

Special attention should be directed to a comparison of the C(6)-N length, 1.310 Å, and C(6)-N barrier to rotation, $\Delta G^\ddagger(0^\circ) = 17.9 \text{ kcal mole}^{-1}$ ($E_a = 20.9 \text{ kcal mole}^{-1}$).² The distance is at the lower end of the range of values usually found for amides⁶ and the E_a is at the upper extreme of the typical amide values.⁷ Both of these quantities suggest that the amount of C=N character in (III) is probably greater than the 40% usually quoted for amides.⁸

The C(3)-C(4) and C(4)-C(5) bonds lengths in (III) together with the previously reported n.m.r. coupling constants, $J_{34} 3.1 \text{ Hz}$ and $J_{45} 4.5 \text{ Hz}$,⁵ provide a good opportunity to check the supposed vicinal proton coupling constant-bond length relationship for five-membered rings.^{2,9,10} The structural and coupling constant data for 6,6-dimethylpentafulvene^{10,11} and cyclopentadiene¹² give $\Delta d/\Delta J = |d_{34} - d_{45}|/(J_{34} - J_{45})$ ratios of 0.040 and 0.041 Å Hz⁻¹, respectively, whereas the much smaller value of 0.014 Å Hz⁻¹ is calculated for (III). In view of the substantial difference between these $\Delta d/\Delta J$ ratios, we would urge caution in the use of such relationships until a time when possible pitfalls are more clearly defined.¹⁰

We are grateful to the National Science Foundation for support of this work. Computer time was made available, in part, through the facilities of the Computer Science Centre, University of Maryland.

(Received, December 15th, 1970; Com. 2170.)

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