# The Molecular Structure of 1,1-Dimethyl-3-Phenylpyrazolium-5-Oxide

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The molecular structure of 1,1-dimethyl-3-phenylpyrazolium-5-oxide has been determined by a single crystal x-ray diffraction study. The crystals are monoclinic, space group $P2_1/a$, with unit cell dimensions a = 12.630 (5) Å, b = 6.644 (1) Å, c = 12.486 (5) Å, $\beta$ = 99.17 (2)°. The final R value was 0.049 for 2930 reflections. The bond lengths and angles suggest that a significant contribution to the structure is made by a resonance form in which one of the ring bonds does not exist. No close intermolecular approaches were found.

## INTRODUCTION

The crystal structure of 1,1-dimethyl-3-phenylpyrazolium-5-oxide, which will subsequently be referred to as DPPO, was determined using peak height measurements of most reflection intensities, which were converted to integrated intensities by the use of an empirically developed conversion function.

Crystals of DPPO were supplied by Henery-Logan and Keiter (1) who isolated it as an unexpected minor by-product in the preparation of the dimethylhydrazone of ethyl benzoylacetate by reaction (1).
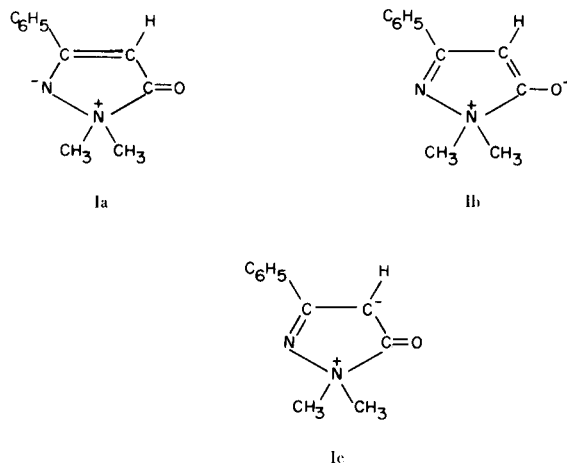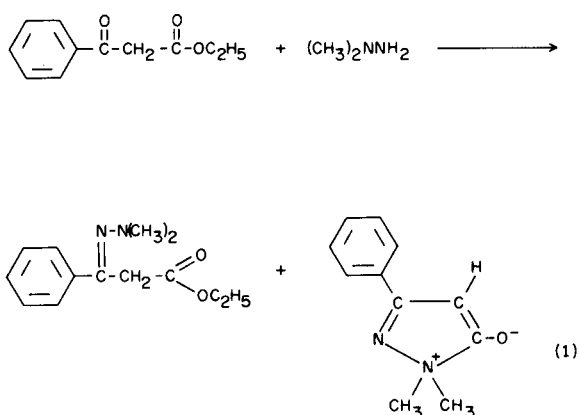


FIGURE I

Proposed Structures for 1,1-Dimethyl-3-phenylpyrazolium-5-Oxide

The suggested structure may be written following conventional rules in three forms, shown in Figure I, which differ only in the placement of the negative charge and two double bonds. Based on IR and NMR studies, Henery-

Logan and Keiter suggested that the best representation of the structure was a resonance hybrid of Ia and Ib.

Pyrazoline rings containing a positively-charged nitrogen atom have been reported by Sokolova and various co-workers (2a-c), but, according to their proposed structure, the charge is located on the nitrogen atom in the $\beta$-position relative to the carbonyl group, while the positive charge is located on the nitrogen $\alpha$ to the carbonyl in DPPO. The bonding and ring structure proposed for DPPO appear to be unique in the chemical literature and, therefore, the structure determination was undertaken in order to investigate the effects of this quaternary nitrogen atom on the pyrazole ring system.

An additional factor of interest is that DPPO is a structural isomer of the antipyretic drug, antipyrine, which has been studied crystallographically both as the *p*-bromo derivative (3) and in various metal complex ions (4a-c).

## EXPERIMENTAL

DPPO was recrystallized from cyclohexane, the crystals forming colorless needles, elongated along the b-axis, and showing well-developed (100) and (001) faces. Unit cell dimensions were

refined by least squares based on fifteen accurate measurements of $2\theta$ for intense reflections. Intensity measurements were made on a General Electric XRD-6 diffractometer with Datex automation. A pulse height selector was used to mitigate the effects of white radiation. The crystal data for DPPO are summarized in Table I.

A total of 5416 individual measurements of 2930 independent reflections were used in the data processing. All reflections in the quadrant of reciprocal space for which k was negative and $\ell$ was positive were measured once by the stationary crystal-stationary counter method. This technique measures only the peak height intensity, not the integrated intensity of the reflection. In order to develop an empirical conversion function, reflections for which peak-to-background ratio was greater than four, or the signal-to-noise ratio was greater than 20, were remeasured by both stationary crystal-stationary counter and moving crystal-moving counter methods. A total of 1049 such comparisons were made. Equation (1), which was developed by a linear least squares treatment of the

$$I_s = I_p \times (3.5583 - 4.1193t + 12.2338t^2 + 1.1353t^3)  \quad (1)$$

comparisons, was used to convert the peak height intensity $I_p$ to the integrated intensity $I_s$. The symbol t represents the tangent

## TABLE I

## Crystal Data

1,1-Dimethyl-3-phenylpyrazolium 5-oxide, $C_{11}H_{12}N_2O$: f.w. 188.23; m.p. 135.0-135.5°.

Monoclinic, a = 12.630 ± 0.005 Å, b = 6.644 ± 0.001 Å, c = 12.486 ± 0.005 Å, $\beta$ = 99.17 ± 0.02°.

Volume of unit cell = 1034 ± 1 $Å^3$.

Calculated density = 1.208 ± 0.001 g/$cm^3$ (Z = 4)

$MoK_\alpha$ radiation ($\lambda$ = 0.71069 Å), Nb filter.

Crystal size 0.1 x 0.2 x 0.6 mm.

$\mu$ ($MoK_\alpha$) = 0.56 $cm^{-1}$.

2930 reflections measured (1648 observed at $3\sigma$ level) to 60° $2\theta$.

Systematically absent reflections: h0$\ell$ for h = 2n + 1; 0k0 for k = 2n +1.

Space group $P2_1/a$ ($C_{2h}^5$).

of theta. The precision of the conversion is shown by the "index of reliability" defined by Equation (2), where

$$i.r. = \frac{I_{os} - I_s}{I_s}  \quad (2)$$

i.r. is the index of reliability, $I_{os}$ is the observed integrated intensity, and $I_s$ is the integrated intensity calculated by Equation (1). The summations are made over all the peak-to-scan comparisons. For DPPO, the index of reliability was 0.031, suggesting that the conversion was precise to an average of about 3%.

After a decay correction was applied to compensate for variations in the standard reflections, all measurements of symmetrically equivalent reflections were averaged. Intensities of symmetrically equivalent reflections generally agreed with each other within ± 5%. Relative structure factor amplitudes ($F_{rel}$) were calculated for all reflections. Lorentz and polarization corrections were applied, but absorption was neglected. Weights for use in least

squares refinement were calculated for each $F_{rel}$ by Equation (3), where K is the greater of $0.005F_{rel}$ and the statistical standard deviation of $F_{rel}$. The values of the atomic scattering factors for

$$weight = \frac{0.4}{K}  \quad (3)$$

C, N, and O were taken from the International Tables (5), and the scattering factors of Stewart, Davidson, and Simpson (6) were used for hydrogen.

## STRUCTURE SOLUTION AND REFINEMENT

Quasi-normalized structure factor amplitudes, or E's, were calculated for all reflections (7). A total of 357 reflections had E's greater than 1.5. These were used to determine phase relationships using Karle and Hauptmann's sigma-2 relationship (8). The phases of all of the 45 reflections with the highest E's were found by symbolic addition (9) to depend only upon the phases of three reflections (0$\overline{9}$4, 2$\overline{8}$3, and 7$\overline{3}$7). These three reflections were arbitrarily assigned a positive phase as a means of fixing the origin of the unit cell. Additional phase relationships within the set of the 45 highest E's were used, whenever possible, to generate phases for other reflections with E greater than 1.5. All phases which could be determined with a probable accuracy of 0.92 or higher were accepted. Two-hundred and four additional phases were thus determined, giving a total of 249 phases determined out of the 357 E's above 1.5. All but three of these phases were confirmed by a calculated F based on the positional and thermal parameters from the final structure solution.

Using the 249 assigned and determined phases, an E-map was computed. All carbon, nitrogen, and oxygen atoms were readily found, and formed a chemically resonable molecule which agreed with the proposed structure. None of these atomic positional parameters was altered by more than 0.3 Å during the refinement of the structure.

$$R = \frac{\Sigma ||F_c| - |F_o||}{\Sigma |F_o|}  \quad (4)$$

The initial structure for DPPO gave a value of 0.48 for R as defined in Equation (4). The parameters of the structure were refined by six cycles of full-matrix least squares (FMLS), reducing R to 0.12. At this point, a difference Fourier map revealed the positions of all the hydrogen atoms. Refinement of all positional and thermal parameters (using anisotropic temperature factors for non-hydrogen atoms, and isotropic t.f.'s for hydrogen atoms) lowered R to 0.078.

The three strongest reflections, all of which had low values of theta, now calculated between 8 and 18% greater than their observed values. These discrepancies were attributed to secondary extinction, and the three reflections were removed from the refinement. Additional cycles of FMLS reduced R to 4.9%. No parameter was shifted in the last cycle by an amount greater than 0.23 of its estimated error.

Final values of the positional and thermal parameters are given in Table II. The anisotropic temperature factors are of the form $exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}\ell^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}h\ell a^*c^* + 2B_{23}k\ell b^*c^*)]$. Figure II is a perspective drawing of the molecule made with the program ORTEP (10) using a Calcomp 650 Plotter. Figure III shows the bond lengths and bond angles for the final structure. A listing of the final calculated and observed structure factors is available from the authors upon request.

TABLE II

Atomic Positional and Thermal Parameters for 1,1-Dimethyl-3-Phenylpyrazolium-5-Oxide

(x, y, and z are multiplied by $10^4$; standard deviations in the last place are in parentheses)

| Atom | x | y | z | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ | B (isotropic) |
|---|---|---|---|---|---|---|---|---|---|---|
| O | 1081 (1) | 2233 (2) | 5180 (1) | 5.50 (6) | 6.53 (8) | 3.58 (6) | 0.10 (5) | -0.16 (5) | 1.64 (5) | 5.05 |
| N (1) | 0144 (1) | 2474 (2) | 3364 (1) | 3.47 (6) | 3.35 (6) | 3.14 (6) | -0.08 (5) | 0.60 (5) | 0.25 (5) | 3.32 |
| N (2) | 0251 (1) | 3716 (2) | 2424 (1) | 3.66 (6) | 3.65 (6) | 2.79 (6) | -0.64 (5) | 0.32 (5) | 0.30 (5) | 3.34 |
| C (1) | 1087 (1) | 4856 (2) | 2758 (1) | 2.52 (6) | 2.91 (7) | 3.01 (7) | 0.26 (6) | 0.36 (6) | -0.47 (6) | 2.81 |
| C (2) | 1580 (1) | 4569 (3) | 3842 (1) | 2.81 (7) | 4.39 (9) | 3.22 (8) | -0.24 (7) | -0.17 (7) | -0.08 (7) | 3.41 |
| C (3) | 1052 (1) | 3115 (3) | 4306 (1) | 3.14 (7) | 4.44 (9) | 3.25 (8) | 0.61 (7) | -0.12 (6) | -0.01 (7) | 3.57 |
| C (11) | 1422 (1) | 6299 (2) | 1980 (1) | 2.81 (7) | 2.86 (7) | 2.98 (7) | -0.03 (6) | 0.53 (5) | -0.45 (6) | 2.88 |
| C (12) | 0762 (1) | 6675 (3) | 0999 (1) | 3.57 (8) | 3.81 (9) | 3.28 (8) | -0.44 (7) | 0.34 (6) | -0.10 (7) | 3.55 |
| C (13) | 1062 (2) | 8022 (3) | 0272 (1) | 5.11 (10) | 4.58 (10) | 3.66 (9) | -0.34 (8) | 0.41 (8) | 0.46 (8) | 4.41 |
| C (14) | 2022 (2) | 9033 (3) | 0504 (2) | 5.88 (11) | 4.08 (10) | 4.53 (10) | -0.96 (8) | 1.67 (9) | 0.22 (8) | 4.77 |
| C (15) | 2679 (2) | 8683 (3) | 1472 (2) | 4.13 (9) | 4.43 (9) | 5.27 (10) | -1.28 (8) | 1.45 (8) | -0.68 (9) | 4.59 |
| C (16) | 2388 (1) | 7331 (3) | 2211 (1) | 3.34 (7) | 4.02 (9) | 3.79 (8) | -0.39 (7) | 0.50 (6) | -0.51 (7) | 3.71 |
| C (21) | -0923 (1) | 2825 (4) | 3687 (2) | 3.46 (9) | 6.13 (13) | 4.67 (11) | -0.22 (9) | 1.07 (8) | 0.90 (10) | 4.63 |
| C (22) | 0279 (2) | 0332 (3) | 3074 (2) | 7.65 (15) | 3.14 (10) | 5.71 (12) | -0.35 (9) | 1.97 (12) | 0.03 (9) | 5.16 |
| H (1) | 2154 (12) | 5276 (22) | 4185 (11) | | | | | | | 4.2 (4) |
| H (2) | 0071 (11) | 5962 (22) | 0835 (10) | | | | | | | 4.0 (3) |
| H (3) | 0604 (12) | 8183 (24) | -0404 (13) | | | | | | | 5.0 (4) |
| H (4) | 2171 (13) | 10008 (26) | -0060 (13) | | | | | | | 6.2 (5) |
| H (5) | 3366 (13) | 9390 (25) | 1662 (12) | | | | | | | 5.7 (4) |
| H (6) | 2864 (11) | 7113 (22) | 2921 (12) | | | | | | | 4.6 (4) |
| H (11) | -1464 (13) | 2416 (27) | 3060 (14) | | | | | | | 5.9 (5) |
| H (12) | -0963 (14) | 4273 (30) | 3848 (14) | | | | | | | 6.1 (5) |
| H (13) | -0943 (12) | 1954 (26) | 4355 (14) | | | | | | | 5.9 (4) |
| H (21) | -0282 (16) | -0012 (28) | 2438 (16) | | | | | | | 7.7 (6) |
| H (22) | 0215 (14) | -0528 (29) | 3695 (15) | | | | | | | 6.8 (5) |
| H (23) | 1000 (17) | 0300 (29) | 2851 (16) | | | | | | | 8.4 (6) |
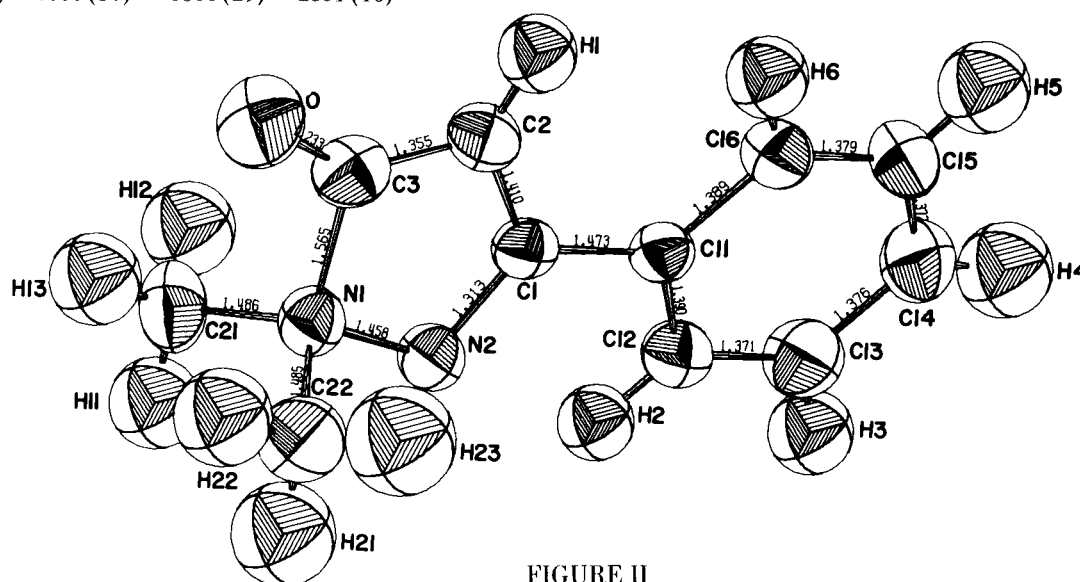


FIGURE II

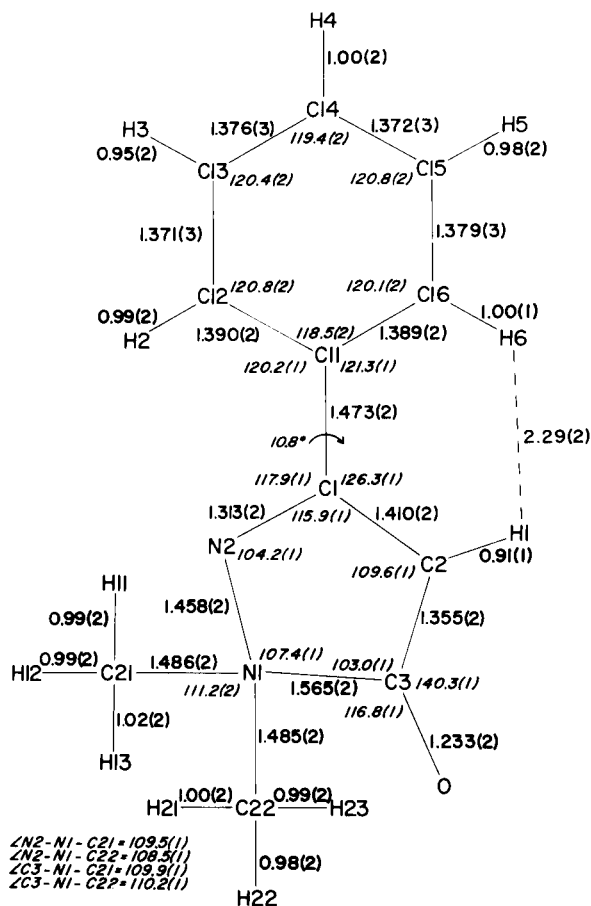ORTEP Drawing of 1,1-Dimethyl-3-Phenylpyrazolium-5-Oxide

FIGURE III

Bond Lengths and Angles for 1,1-Dimethyl-3-Phenyl-pyrazolium-5-Oxide

A Fourier map of the difference between the observed and calculated electron densities was made using the final values of the calculated structure factors. No differences in electron density greater than 0.2 electron/$\text{Å}^3$ appeared at any point in the unit cell, indicating that the model represented by the parameters in Table II agrees very closely with the observed electron density.

## DISCUSSION OF THE STRUCTURE

Considered as a whole, the DPPO molecule is very nearly planar. The six atoms of the phenyl ring lie within 0.003 Å of the least squares plane which they determine. The five atoms which make up the pyrazole ring all fall within 0.005 Å of their least squares plane. A chi-squared test gave values of 0.15 and 0.58, implying that the two rings are planar with probabilities greater than 99% and 95% for the phenyl and pyrazole rings, respectively. The equations for these two planes, along with the distance of each atom from them, are given in Table III. The method of calculation is that of Schomaker, Waser, Marsh, and Bergman (11). The plane is defined by Equation (5), in which p,q,r, and s are the constants given in Table III and x,y, and z are

$$px + qy + rz = s \tag{5}$$

fractional coordinates of a point in the unit cell which lies on the plane.

The two planes form an angle of 10.8 degrees with each other. This angle is due primarily to rotation around the C (1) –C (11) bond, since the angle C (1) –C (11) –C (14) is 179.10°. This slight bowing does not appear to be significant, for many structures consisting of two or more rings bonded to each other show a similar feature. The most reasonable explanation appears to be that the bending is due to the packing of the molecules into the unit cell.

The possibilities of conjugation between the double bond systems of the two rings might lead one to anticipate that they would be coplanar. However, the distance 2.29 Å from H (1) to H (6) is less than twice the Van der Waals radius of hydrogen of 1.2 Å reported by Pauling (12). This suggests that steric factors prevent the coplanarity of the phenyl and pyrazole rings. Dihedral angles of 40° and 63° have been reported respectively for bromo-antipyrine (3) and several metal complexes of antipyrine (4). An angle of 28° was found in 3-(p-bromophenyl)sydnone (13). None of these reported structures gave hydrogen atom locations which were found experimentally, so the likelihood of hydrogen atoms being in contact cannot be estimated. In the structure of 1-phenyl-tetrazole (14), the dihedral angle was reported to be 12 degrees. In this case a hydrogen atom bonded to a carbon atom alpha to the phenyl ring is located in the plane of the five-member ring, similar to DPPO. Even smaller angles of 8° and 5° were reported for another similar case, 1,3-diphenyl-$\Delta^2$-pyrazoline (15). There the carbon atoms alpha to the phenyl rings are tetrahedral, thus removing the hydrogen atoms from the plane of the five-membered ring, which would allow a greater degree of coplanarity.

Additional evidence for lack of conjugation between the phenyl and pyrazole rings is the C (1) –C (11) bond length of 1.473 (2) Å. This value compares favorably with lengths for single bonds between $sp^2$ carbon atoms in cyclooctatetraene (1.462 Å) (16) and 1,3-butadiene (1.483 Å) (17). Dewar and Schmeising (18) have suggested that the value of 1.476 Å which they calculated for the $sp^2-sp^2$ single bond between carbon atoms is probably a little large, while Lide (19) asserted that the range 1.47-1.48 Å might be a good "guess". It seems clear that whatever conjugation between the rings is present in DPPO does not shorten C (1) –C (11) significantly

The geometry of the five-member ring is as expected. Reference to Figure III shows N (1) in the anticipated tetrahedral configuration. The bonds from N (1) to C (21), C (22), and N (2) are all close to normal single bond values. A single bond from a tetrahedral carbon to a tetrahedral nitrogen is reported to be 1.479 (5) Å, and the N–N single bond has been reported as 1.451 (5) Å between $sp^2$ atoms, and 1.41 (2) Å between $sp^3$ atoms (20). A length of 1.315 Å has been found for the C–N bond in s-triazine (21), in which symmetry requires that the C–N bond character be 1.5. The N (2) –C (1) bond in DPPO is 1.313 (2) Å and may also be assumed to have a bond character of 1.5. C (1) –C (2) and C (2) –C (3) bonds both have lengths which are intermediate between the 1.335 (10) Å which Lide (19) reports for a double bond between trigonal carbon atoms and the approximate figure of 1.47 Å for a single bond, although C (2) –C (3) is rather close to the double bond value. The length of 1.233 (2) Å for the bond from C (3) to O is slightly longer than the generally accepted value of 1.215 (5) Å for carbonyl bonds in a conjugated system or in aldehydes and ketones (20).

All of the interior angles of the pyrazole ring are generally within the range of values found in five-member rings. The angle at N (1) is, not surprisingly, close to the tetrahedral angle of 109°28'. The smaller angle at N (2) is consistent with observations in cases such as s-triazine (21) and s-tetrazine (22), in which

nitrogen atoms having a lone pair of electrons show interior angles which are smaller than the 120° angle expected in a six-member ring.

The N (1) –C (3) bond length of 1.565 Å and the C (2) –C (3) –O angle of 140.3° are both highly unusual. The only comparable C–N bond lengths known to have been reported are one of 1.58 ± 0.06 Å, in the hydrobromide of 3-methoxycarbonyl-trans-3,5-dimethyl-$\Delta^1$-pyrazoline (23) and one of 1.64 ± 0.02 Å in the alkaloid retusamine (24). The large standard deviation in the case of the first compound subjects the significance of the bond length to some doubt. In the retusamine structure, the C–N bond bridges an 8-member ring, forming two five-member rings, and is subject to steric strain. It is reported to be very labile. The bond in DPPO is also easily broken, Keiter reporting that the compound undergoes reaction when it is dissolved in methanol and allowed to stand overnight (1).

Hope and Thiessen (25) have reported a similar situation with a C–O bond in the structures of two bissydnones, in which the average ring C–O bond is 1.41 Å, much longer than the corresponding distance in furan. As in DPPO, their structures showed the angle opposite the long bond to be unusually large, ranging from 136.0° to 136.7°. Sydnones are mesoionic compounds, for which an uncharged resonance form cannot be drawn. Baker and Ollis (26) suggested the existence of polar resonance forms, which, in the case of the sydnones, placed a negative charge on the exocyclic oxygen atom. However, neither the bissydnone structures nor the structure of 3-(p-bromophenyl)sydnone (13) show a lengthening of the exocyclic C–O bond, as would be expected. Hope and Thiessen proposed, in essence, that the cyclic system of $\pi$ electrons exists, accounting for the observed aromatic character of the sydnones, but that the *sigma* bond between the carbon and oxygen atoms involved in the unusual bond has "much less than normal weight", thus accounting for the longer bond.

This possibility does not exist in the case of DPPO, since N (1) does not show a trigonal structure, and thus cannot form $\pi$ bonds. The large C (2) –C (3) –O angle in DPPO suggests that the hybridization around C (3) deviates significantly from the expected $sp^2$ geometry. Indeed, one can imagine a more extreme case in which C (3) actually assumes sp hybridization. The C (2) –C (3) –O angle would then be 180°, and C (2) –C (3) and C (3) –O could both be double bonds. The geometry of a hybrid structure, it should be noted, is not required to be identical to that of any of the contributing forms, either with respect to bond lengths or bond angles. A bond angle may be observed to be substantially different from a theoretical value, as is the case with C (3) of DPPO. However, this cannot justify the exclusion of structures with this theoretical geometry. Specifically, if one admits the
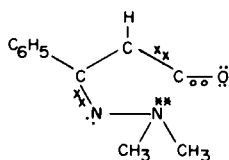


FIGURE IV

Proposed "Ketene" Structure for 1,1-Dimethyl-3-phenylpyrazolium-5-Oxide

— $\sigma$ bonding electron pair
xx $\pi$ bonding electron pair ($\pi$ orbitals perpendicular to plane of paper)
oo $\pi$ bonding electron pair ($\pi$ orbitals in plane of paper)
•• non-bonding electron pair (orbital in plane of paper)
·· non-bonding electron pair (orbitals not specified)

possibility of contributing structures with trigonal ($sp^2$) hybridization at C (3), the observed bond angle forces contributing structures with linear (sp) hybridization to be considered as well.

Dewar and Schmeising (18) observed that the contraction in bond length in passing from an $sp^3$–$sp^3$ single bond (ethane) to an $sp^3$–sp single bond (methylacetylene) is 0.082 Å, and the change in going from an $sp^3$–sp single bond to an sp–sp single bond (biacetylene) was 0.080 Å. This suggests that the covalent radius of carbon changes with hybridization, and that a change

TABLE III

1,1-Dimethyl-3-phenylpyrazolium-5-Oxide

Least Squares Planes of Equation $px + qy + rz = s$

|   | Plane I | Plane II |
|---|---|---|
| p | 6.675 | 8.328 |
| q | -4.876 | -4.581 |
| r | -6.310 | -5.008 |
| s | -3.375 | -2.703 |

| Atom | Distance from Plane in Ångstroms | |
|---|---|---|
| O | -0.261 | -0.013 |
| N (1) | 0.142 | 0.005 (a) |
| N (2) | 0.200 | -0.004 (a) |
| C (1) | -0.009 | 0.002 (a) |
| C (2) | -0.223 | 0.002 (a) |
| H (1) | -0.401 | -0.016 |
| C (3) | -0.159 | -0.004 (a) |
| C (11) | 0.003 (a) | 0.010 |
| C (12) | 0.002 (a) | -0.220 |
| H (2) | -0.012 | -0.387 |
| C (13) | 0.000 (a) | -0.223 |
| H (3) | 0.042 | -0.341 |
| C (14) | 0.001 (a) | -0.003 |
| H (4) | -0.019 | -0.043 |
| C (15) | -0.001 (a) | 0.219 |
| H (5) | -0.006 | 0.373 |
| C (16) | -0.001 (a) | 0.226 |
| H (6) | -0.025 | 0.367 |
| C (21) | -0.946 | -1.206 |
| H (11) | -0.711 | -1.155 |
| H (12) | -1.780 | -1.983 |
| H (13) | -0.955 | -1.158 |
| C (22) | 1.459 | 1.244 |
| H (21) | 1.654 | 1.253 |
| H (22) | 1.444 | 1.273 |
| H (23) | 2.097 | 1.971 |

(a) Atom which was used to define the least squares plane.

from sp³ to sp hybridization is accompanied by a reduction of approximately 0.08 Å in bond lengths around that atom. On the assumption that the covalent radius of an atom is a linear function of its s-character, a value of 0.745 Å may be calculated for the covalent radius of sp² carbon. The sp covalent radius for carbon is 0.690 Å. Thus one might expect a shortening of approximately 0.055 Å from bond lengths to an sp² carbon when the hybridization changed to sp.

The longer bond in carboxylic acids and esters is reported to be 1.321 ± 0.005 Å (20). This value represents the single bond length between sp² carbon and oxygen. Subtraction of 0.055 from this value leaves 1.257 Å for an estimate of the single bond length from sp carbon to oxygen. The sp C—O double bond in ketene has been measured at 1.161 Å (27). In DPPO, the C (3) —O bond is intermediate between these two values, but closer to the single bond length.

Following the example of Hope and Thiessen (25), a structure may be drawn for DPPO which has sp hybridization at C (3), and no bond from C (3) to N (1). This "ketene" structure is shown in Figure IV. No formal charges are necessary on either N (1) or O. N (1) may be considered to be sp³ hybridized with a lone pair of electrons in one orbital. The electrons which form the π-bond between C (3) and O are located in p orbitals which are coplanar with the five-member ring. These electrons may be conceived of as normally delocalized over C (3) and O, but these may also be considered as localized on O, giving it a negative charge, and making C (3) —O a single bond. In this extreme case, which is identical to Ib, consideration of the geometry of the DPPO molecule shows that the empty p orbital on C (3) points approximately toward the sp³ orbital on N (1) which contains the electron pair, and the formation of an sp³—p sigma bond may be possible.

The preceding is not meant to suggest that this extreme situation represents a possible structure, but only to demonstrate that a reasonable distribution of electrons may be drawn for the extreme case of sp hybridization at C (3). Consequently, the true situation may well be either a form of hybridization at C (3) which is intermediate between sp and sp², or a resonance hybride of various extreme structures.

The argument may also be based on the increased polarizability of p orbitals. The presence of the positive nitrogen adjacent to the carbonyl group (assuming an idealized sp² hybridization at C (3)) would have the same effect as a very electronegative substituent, and the sp² orbital shared with N (1) would become polarized, withdrawing p character from the other two C (3) hybrid orbitals. As the s character in the sp² orbitals on C (3) directed toward C (2) and O increases, the bonds will become shorter. Similarly, the increase in p character in the sigma bond with N (1) would lengthen the bond.

It is interesting to note that many heterocyclic ketones show a small opening of the angle opposite the heteroatoms. Some recently determined structures (in addition to DPPO and the bissydnones) which show this phenomenon, and the angle (or angles) opposite the heteroatom or atoms are d-galactono-γ-lactone, 128.5° (28), β-d-glucurono-γ-lactone, 128.9° (29), β-bromopicrotoxin, 129.5° and 129.1° (30), N-methyl-4-phenylisoxazolin-5-one, 135.5° and 133.0° (31), N-methyl-3-phenyl-4-bromo-isoxazolin-5-one, 135.0° (32), 3-phenylisoxazolin-5-one, 131.2° (33), and 3-methylpyrazolin-5-one, 132.2° (34).

The existence of the ketene structure appears to be even more likely when attempts are made to deduce the relative contributions of forms Ia, Ib, and Ic from the bond lengths found in DPPO. The bond character of 1.5 which was assigned to N (2) —C (1) suggests that the contribution of form Ia, which is related to 3-pyrazoline,

is 50%, since it is the only proposed contributing structure which has a single bond in this position. The total contribution of structures Ib and Ic must then be the remaining 50%. Pauling's equation (35) may be used to calculate a bond character of 1.4 for C (1) —C (2). Since structure Ia is also the only one which has a double bond between these two atoms, this indicates a contribution of 40% for the 3-pyrazoline form of DPPO.

The disagreement between the two figures is of marginal significance, at best. The lengths of bonds having bond characters of 1.4 and 1.5 differ by 0.016 Å for C—C bonds, or, in the case of C (1) —C (2), about eight times the standard deviation in the bond length. The standard deviations in the bond lengths are developed from the corresponding values for the estimated standard deviations (esd) in the positional parameters, which are calculated from the diagonal elements of the inverse of the normal equations matrix used in the least squares refinement. Such values tend to be optimistic, and should be considered to be a lower boundary for the esd. Consequently, caution should be observed in attributing chemical importance to structural differences which are less than at least five times the esd.

Contributions for the pyrazole form Ib may be calculated from the bond lengths found for C (2) —C (3) and C (3) —O, which are respectively double and single only in this structure. By the above method, a bond character of 1.8 is found for C (2) —C (3) suggesting a contribution of 80%. However, the carbonyl bond shows little lengthening from its normal value, which implies a negligible contribution for Ib. The 2-pyrazoline structure Ic has single bonds for C (1) —C (2) and C (2) —C (3), which complicates the analysis further.

These conflicts may be resolved if the additional contributing structure shown in Figure IV is proposed. A bond length vs. bond character curve may be developed from the C—N single bond length of 1.47 reported by Pauling (36), the length of the C—N bond of character 1 1/3 in melamine, 1.346 Å(37) and 1 1/2 bond in s-triazine. If this curve is smoothly extrapolated, the length observed for N (1) —C (3) corresponds to a bond character of 0.85, which suggests a contribution of approximately 15% for the ketene form of DPPO.

## CONCLUSION

Averaging the contributions of the 3-pyrazoline form Ia calculated from the lenghts of bonds N (2) —C (1) and C (1) —C (2) gives a contribution of 45% for this form. The short C (2) —C (3) bond suggests little single bond character, so no additional significant single bond contribution from the 2-pyrazoline form Ic is suggested. This leaves a contribution of 40% for the pyrazole structure Ib originally proposed, and 15% for the ketene form.

Crystallographic computations were carried out using XRAY67 (38) on a Univac 1108 computer. Computer time was provided by the Computer Science Center, University of Maryland, under Grant NSG398 from the National Aeronautics and Space Administration. Use of the diffractometer was provided through the courtesy of the biochemistry division of the Walter Reed Army Institute of Research.

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