

tively at the 3-benzyloxy group to yield almost quantitatively the 7-monobenzoates. 7(α)-Benzyloxycholesterol and 7(α)-benzyloxystigmasterol thus

prepared have been converted to the corresponding free 7-dehydrosterols.

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The Dipole Moment of a Free Radical

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Before the development of our present ideas of resonance, the dipole moments of α,α -diphenyl- β -picrylhydrazine and the free radical, α,α -diphenyl- β -picrylhydrazyl, were measured,¹ as were those of triphenylchloromethane and triphenylcarbinol.² The moment value found for triphenylchloromethane was close to those of the butyl chlorides, while that for triphenylcarbinol was about 0.4 higher than the moments of most of the alcohols. Moment values for 1,1,1-triphenylethane,³ triphenylmethane,^{4,5} and tri-*p*-nitrophenylmethane⁵ showed no abnormality. Absence of marked abnormality in the moments of these molecules, which are closely related to free radical-forming structures, is to be expected in view of the fact that the resonating structures particularly responsible for the stabilization of the free radicals cannot contribute to these structures. Karagunis and Jannakopoulos⁶ have recently found zero moment for the solutes in solutions of hexaphenylethane and tribiphenylmethyl and have attributed the absence of moment to the existence of the free radicals in symmetrical, planar structures.

In the present investigation, the early measurements upon α,α -diphenyl- β -picrylhydrazine and α,α -diphenyl- β -picrylhydrazyl have been repeated. The two substances were prepared by methods given in the literature.^{7,8}

Experimental Results

The dipole moments were obtained by means of the apparatus and methods previously described,⁹ the dielectric constants of benzene solutions of mole fractions, c_2 , being measured at a

frequency of 520 kilocycles and the densities, d , of the solutions being determined with an Ostwald-Sprengel pycnometer. These data are listed in Table I, together with the polarizations, P_2 , calculated for the solute, the values of P_∞ obtained by extrapolation of the P_2 values, the molar refractions for the D sodium line, MR_D , calculated as the sums of atomic and group refractions, and the dipole moments, μ .

TABLE I
DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AND POLARIZATIONS AT 25° AND DIPOLE MOMENTS

c_2	ϵ	d	P_2
α,α -Diphenyl- β -picrylhydrazine			
0.00000	2.2756	0.87321	...
.00265	2.3249	.87768	355
.00556	2.3824	.88264	361
.00659	2.4017	.88417	361
P_∞ , 370; MR_D (calcd.), 106; μ , 3.59×10^{-18}			
α,α -Diphenyl- β -picrylhydrazyl			
.000000	2.2726	.87313	...
.000792	2.3002	.87455	587
.001558	2.3272	.87600	588
.003292	2.3854	.87903	574
.004927	2.4367	.88168	558
.005351	2.4537	.88242	564
.009027	2.5768	.88912	550
P_∞ , 600; MR_D (calcd.), 105; μ , 4.92×10^{-18}			

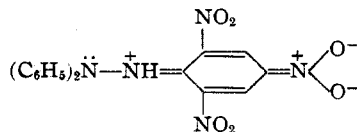
Discussion of Results

The moment value 3.59 in Table I for α,α -diphenyl- β -picrylhydrazine is distinctly larger than the value 3.08 found by Wolf, but the value 4.92 for the free radical is in excellent agreement with Wolf's value, 4.88. The molecules of hydrazine, phenylhydrazine, α,α -, and α,β -diphenylhydrazine have moments between 1.53 and 1.87.¹⁰ Since the three nitro groups of the picryl group are symmetrically located around the ring, their moments, in the absence of complicating effects, should cancel as do the similar moments in 1,3,5-trinitrobenzene, which has zero moment. In the

- (1) Wolf, Diplomarbeit, Karlsruhe, 1930.
- (2) Smyth and Dornte, THIS JOURNAL, **53**, 545 (1931).
- (3) Smyth and Dornte, *ibid.*, **53**, 1296 (1931).
- (4) Lautsch, *Z. physik. Chem.*, **B1**, 115 (1928).
- (5) Bergmann, Engel and Wolff, *ibid.*, **B17**, 81 (1932).
- (6) Karagunis and Jannakopoulos, *ibid.*, **B47**, 343 (1940).
- (7) Goldschmidt, *Ber.*, **55**, 628 (1922).
- (8) Turkevich and Selwood, THIS JOURNAL, **63**, 1077 (1941).
- (9) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939); THIS JOURNAL, **61**, 3063 (1939).

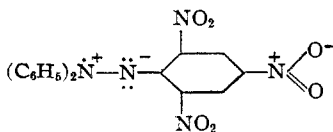
- (10) Audrieth, Nespital and Ulich, *ibid.*, **55**, 673 (1933).

absence, then, of these complicating effects, α, α -diphenyl- β -picrylhydrazine should have a moment close to that of α, β -diphenylhydrazine, about 1.5. The fact that the observed moment is more than twice as large as this value points to resonance with contributions from polar structures somewhat analogous to those which raise the moment of *p*-nitroaniline considerably above the vector sum of its group moments. The most polar of these structures would be



The two analogous structures with a double bond to an ortho instead of the para nitrogen would have smaller moments because of the shorter distance between the charges. Penney and Sutherland¹¹ succeeded in calculating the moment value of hydrazine on the assumption that the two halves of the molecule were so rotated relative to one another around the nitrogen-nitrogen bond as to occupy a position of minimum potential energy. Although the moments of the phenylhydrazines are close to that of the unsubstituted compound, any such calculation for this compound with its altered valence angles would be even more speculative than that for hydrazine, too speculative to have any value. It is evident, however, that these polar structures make large contributions to the structure of α, α -diphenyl- β -picrylhydrazine.

Measurements of magnetic susceptibility^{8,12,13} have shown that α, α -diphenyl- β -picrylhydrazyl exists even at liquid air temperatures almost wholly as the free radical, which is apparently stabilized by resonance¹⁴ among such structures as



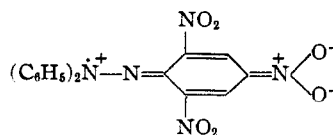
(11) Penney and Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934).

(12) Müller, Müller-Rodloff and Bunge, *Ann.*, **520**, 235 (1935).

(13) Allen and Sugden, *J. Chem. Soc.*, 440 (1936).

(14) Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p. 328.

and



The second of these structures and the two analogous ones with the double bond to an ortho instead of to the para nitro group would have even larger moments than the somewhat similar structures for the hydrazine. The increased resonance among these polar structures evidenced by the fact that the resonance energy is so great as to keep the compound a free radical must enlarge the contributions of these highly polar structures beyond those of the somewhat similar structures for the hydrazine. The increase, 1.3, in the moment, of the hydrazyl as compared to the hydrazine gives additional evidence of the increase in the contributions of the polar structures to the structure of the free radical. It would appear that, while the absence of moment in triphenylmethyl⁶ may be attributed to the symmetrical distribution of the odd electron among different structures, in which the valences of the trivalent carbon are symmetrically arranged in a plane, the increase in the moment of the hydrazyl over that of the hydrazine results from increased resonance among structures of greater polarity. No evidence is given by the moment of either free radical of the localization of the odd electron in such a way as to give rise to a dipole similar to those commonly associated with bonds.

Summary

The dipole moments of α, α -diphenyl- β -picrylhydrazine and of the free radical, α, α -diphenyl- β -picrylhydrazyl, have been measured. The great increase in the moment of the hydrazine over those of the phenyl hydrazines shows resonance with large contributions from polar structures. The further increase in the moment of the free radical over that of the hydrazine corresponds to the increased resonance among polar structures which stabilizes the free radical. No evidence is found of the localization of the odd electron of the free radical in such a way as to form a dipole similar to those commonly associated with bonds.

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