

the main features of the spectrum are due to hyperfine interaction with protons on carbon atoms 1, 3, 6, 8 of II (each unpaired electron in II being effectively restricted to one-half of the molecule) while the additional splittings arise from the protons on 2, 4, 5, 7.

Ether solutions of the green form did not reveal any absorption at -77° . However, on warming to -46° a resonance was observed which disappeared as the color disappeared. Possibly some complexing occurs at the lower temperature leading to broadened lines which could not be detected.

A dark green solid may be obtained from I by sublimation onto a glass surface cooled by liquid nitrogen. At -197° this material exhibited a resonance (line width 14 gauss). After one hour at room temperature the material reverted to the yellow species which did not show e.s.r.⁶

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(6) This e.s.r. examination was kindly performed by Dr. J. P. Gordon.

BELL TELEPHONE LABORATORIES
MURRAY HILL, N. J.

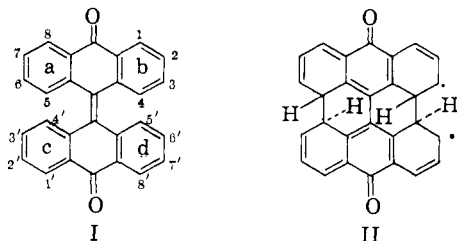
EDEL WASSERMAN

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THE STRUCTURE OF THE THERMOCHROMIC FORM OF BIANTHRONE

Sir:

In solution, yellow $\Delta^{10,10'}$ -bianthrone (I) exhibits a reversible thermochromism involving equilibration with a green form whose concentration increases with temperature.¹ The same green species is obtained by irradiation of the solution at -77° and by the application of pressure to the solid.^{1,2} We propose that the green form is a diradical of which II is one of the resonance structures



In support of II we note that the green form is magnetic.³

We may exclude the possibility that the magnetic species is a diradical in which two planar "anthrone halves" are twisted about a single bond. Harnik and Schmidt's X-ray analysis of I demonstrates that rings a and b are above the plane of the paper, and rings c and d below.⁴ Consequently, a twisted diradical would be stabilized by substituents in the 4 and 4' positions. However, Hirshberg and Fischer's data indicate that the introduction of such

(1) G. Kortüm, *Angew. Chem.*, **70**, 14 (1958), and references cited therein.

(2) E. Wasserman and R. E. Davis, *J. Chem. Phys.*, **30**, 1367 (1959).

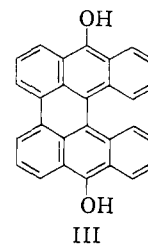
(3) E. Wasserman, *THIS JOURNAL*, **81**, 5006 (1959).

(4) E. Harnik and G. M. J. Schmidt, *J. Chem. Soc.*, 3295 (1954).

groups renders the green form less stable.⁵ The increased lability of II is attributable to steric interactions between the substituents and the d and a rings.

The absence of a betaine structure is demonstrated by the kinetics of the disappearance of the green form at -50° . The rate in ethanol is greater than that in isoöctane by a factor of two.

In neutral solvents, I yields the green form (absorption maximum 6800 Å.) under ultraviolet irradiation at low temperatures. However, pyridine solutions produce a green color with an absorption maximum at 6270 Å. and a shoulder at 5750 Å. which are sensitive to both oxygen and excess I. This is the same band that Brockmann and co-workers have assigned to III, an isomer of II.⁶



Solutions of I react with sodium *t*-butoxide in the absence of light, to yield a red anion. Upon acidification (even methanol is a suitable acid) at -77° , the green form is produced. The formation of the thermodynamically less stable isomer finds precedence in the neutralization of other mesomeric anions.⁷

The piezochromism implies that the green species has a smaller volume than I.

The above data appear to be most compatible with structure II for the green form.

(5) Y. Hirshberg and E. Fischer, *ibid.*, 629 (1953). Data given in Figure 4. The authors do not comment on this effect of substituents.

(6) H. Brockmann, F. Pohl, K. Maier and M. N. Haschad, *Ann.*, **553**, 1 (1942); H. Brockmann and R. Mühlmann, *Chem. Ber.*, **82**, 348 (1949).

(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 565.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
BELL TELEPHONE LABORATORIES
MURRAY HILL, NEW JERSEY

R. B. WOODWARD

EDEL WASSERMAN

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STRUCTURE OF STERCULIC ACID POLYMER. A CYCLOPROPENE REARRANGEMENT

Sir:

Sterculic acid (I)¹ is unstable at room temperature²⁻⁴ and polymerizes with apparent destruction of the cyclopropene group.^{3,4a} We now have established that this polymerization proceeds with ring opening to give the polymeric mixture of compounds IIa-d (where R' and R'' are sterculic acid residues).

(1) For leading references, cf. K. L. Rinehart, Jr., W. A. Nilsson and H. A. Whaley, *THIS JOURNAL*, **80**, 503 (1958).

(2) J. R. Nunn, *J. Chem. Soc.*, 313 (1952).

(3) P. K. Faure and J. C. Smith, *ibid.*, 1818 (1956).

(4) (a) W. A. Nilsson, B.S. Thesis, University of Illinois, 1957; (b) H. A. Whaley, B.S. Thesis, University of Illinois, 1956.