

or without charge-separation.⁸ The excited state linking II and III, on the other hand, must be charge-separated. The only ultraviolet absorption exhibited by these substances above 220 m μ is the $n \rightarrow \pi^*$ band in the 280 m μ region and the rather large extinction coefficients observed indicate considerable interaction in the excited state between the carbonyl group (ketone) and the double bond.^{3,5} This is a result of the favorable orbital overlap imposed by the rigidity of II and III and is possible in II because of the *cis* ring fusion.

The possibility that the rearrangement is the result of normal excitation (singlet) of the ketone carbonyl followed by an internal transfer of energy to the reaction site cannot be discarded. It seems unlikely, however, as an indiscriminate transfer of energy to ring-A would be expected to induce elimination of acetic acid and give rise to the dienone (V) or ultimately to its photodimer (a high-melting solid). Neither could be isolated. Experiments designed to establish this important point in an unequivocal manner are in progress.

The irradiation of *trans*-cinnamyl acetate gave no evidence of acetate migration but instead afforded a dimeric product which appears to be a substituted cyclobutane.

(8) Such a mechanism appears to operate in a type of 1-2 acetate rearrangement. D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

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STERIC EFFECTS ON NITROGEN HYPERFINE COUPLING IN METHYL SUBSTITUTED MONO- AND DINITROBENZENE ANION RADICALS

Sir:

The recent electron spin resonance (e.s.r.) study of an extensive series of *para* substituted nitrobenzene anion radicals has established the dependence of the nitrogen hyperfine coupling constant on the inductive and mesomeric nature of the *para* substituent.¹ We now wish to report hyperfine coupling data for a series of methyl substituted nitrobenzene anion radicals.

Comparison of the nitrogen coupling constant, $|a_N|$, for the anion radicals of nitrobenzene (10.32 gauss), 1,3-dimethyl-2-nitrobenzene (17.8 gauss), and 2,3,5,6-tetramethylnitrobenzene (20.4 gauss) establishes clear evidence of sterically-induced decoupling of the nitro group π -electron system from the aromatic π -electron system. Analogous evidence is available for dinitrobenzene anion radicals. Maki and Geske² have suggested previously that the unusually low nitrogen coupling constant for the anion radical of *p*-dinitrobenzene (1.74 gauss) could be accounted for on the basis of significant mesomeric interaction between the two nitro groups. It is therefore significant that the nitrogen coupling constant for the anion radical of the totally methylated derivative, 1,4-dinitrobenzene, is increased to 8.7 gauss.

The data presented in Table I suggest that the inductive effect of the methyl group is not of

importance in determining the gross trend observed in the distribution of spin density in this series of radicals. The comparatively small effect on $|a_N|$ of introducing a single *ortho*-methyl group as compared to di-*ortho* substitution parallels other chemical observations.³ It is apparent from the decrease of *all* ring coupling constants simultaneously with an increase in the nitrogen coupling constant that the net result of steric interference by *ortho* methyl groups is to localize more and more of the odd electron density on the nitro group to the exclusion of the ring. In this light it is significant that $|a_N|$ observed for the highly hindered compounds approaches the nitrogen coupling constant for various nitroaliphatic anion radicals, 22.9–25.2 gauss.⁴ Successful observation of nitroaliphatic anion radicals demonstrates that the stabilizing influence of the aromatic ring, while considerable, is not necessary to the existence of nitro anion radicals.

TABLE I
COUPLING CONSTANTS FOR ANION RADICALS OF METHYL SUBSTITUTED NITROBENZENES

Methyl position ^b	Coupling constants ^a (absolute value in gauss)			
	a_N	a_o	a_m	a_p
...	10.32	3.39	1.09	3.97
4 ^c	10.79	3.39	1.11	3.98
3,5	10.6	3.29	1.08	3.92
2	11.0	3.12	1.04	3.91
2,3	11.7	2.91	0.99	3.3
2,6	17.8	0.87	...	1.44
2,3,5,6	20.4

^a a_o , a_m and a_p are coupling constants for positions *ortho*, *meta* and *para* to nitro group. For a given position, ring protons and methyl group protons have identical coupling constants within the resolution of our assignments. ^b Nitro group assigned ring position 1. ^c Data from ref. 1. ^d No discrete structure was evident on these lines. In view of the known resolution of the instrument (≤ 0.1 gauss), the coupling constant must be appreciably less than the observed line width of 1.2 gauss.

The trend observed in coupling constants is consistent with a qualitative explanation invoking twisting of the nitro group about an axis lying in the ring. Such a deformation would clearly reduce the coupling between the contiguous π -electron systems. A second possibility, that of deformation of the nitro group from coplanarity with the abutting carbon atom, would also increase the nitrogen coupling constant via the accompanying necessary increase in s-character of the nitrogen orbital involved in the nitro group π -electron system. This increase in s-character would increase the scale of the contact interaction without requiring an increase in spin density. However, for small distortions, it seems likely that the latter mechanism would produce only a slight effect on the coupling with the ring, and thus would not agree with the experimental observations.

E.s.r. data were obtained with an X-band homodyne balanced mixer spectrometer using bolometer detection and 400 cycle audio modulation. The anion radicals were generated electrolytically

(1) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

(2) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

(3) B. M. Wepster in "Progress in Stereochemistry," Vol. 2, edited by W. Klyne and P. B. D. de la Mare, Butterworths Scientific Publications, London, 1958, p. 99.

(4) L. Piette, P. Ludwig and R. N. Adams, private communication.

directly within the microwave cavity by reduction of millimolar solutions of the neutral parent molecule using acetonitrile as solvent.¹ Detailed e.s.r. and polarographic data for compounds in the table as well as several related compounds currently being studied will be presented in detail elsewhere.

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RECEIVED JULY 11, 1961

BIRADICALS IN THE KETYL SERIES¹

Sir:

We have reported previously that the paramagnetic molecules formed on reduction of hexamethylacetone and pentamethylacetone by sodium or lithium are characterized by hyperfine splittings in which each unpaired electron spin is coupled to the nuclei in one ketone molecule and two equivalent alkali metal nuclei.² Dimeric molecules in which the two organic radicals are joined through two equivalent alkali metal ions could account for the observations. Such molecules are biradicals with each electron spin belonging predominantly to one-half of the dimer but sharing the two alkali metal nuclei with the other electron spin. The sharing refers to a time average and does not imply simultaneous presence of the electron spins at a particular site.

We have carried out new experiments with ketyls of the alkaline earths which suggest the formation of biradicals in which the two radicals are joined by a single divalent alkaline earth ion. Reduction of xanthone or benzophenone by magnesium, calcium, or barium in ethereal solvents leads in each case to a single paramagnetic species with hyperfine couplings to the protons in one molecule of the original ketone. The proton coupling constants are slightly dependent on the positive ion, varying monotonically with size of the positive ion. No trace of the dissociated ions is observed. The electron transfer reactions between the dimeric ketyls, both aliphatic and aromatic, and their parent ketones are too slow ($k < 10^5 M^{-1} \text{sec}^{-1}$) to be measured by e.s.r. spectroscopy, while the reaction of the monomeric aromatic ketyls of the alkali metals are very rapid ($k > 10^8 M^{-1} \text{sec}^{-1}$)³

Use of magnesium enriched to 93% of ²⁵Mg yields further evidence bearing on the constitution of the ketyls. In the case of benzophenone magnesium ketyl the expected splitting by one ²⁵Mg nucleus ($I = 5/2$) is observed. The interval between adjacent components is 0.3 gauss. The other ketyls with ²⁵Mg exhibit a broadening of all lines, but no well-resolved ²⁵Mg splitting.

(1) This work has been supported in part by the U. S. Air Force under Contract and in part by an Equipment Loan Contract with O. N. R. Grateful acknowledgment is also made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.

(2) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **82**, 4424 (1960).

(3) F. Adam and S. Weissman, *ibid.*, **80**, 1518 (1958).

The lack of observable coupling between the electronic spin in the biradicals here reported as well as in others previously described is a matter of some theoretical interest.⁴ We are continuing experimental studies of radicals bound together by various metal ions, including tripositive ones, in order to gather further information concerning spin couplings in many electron systems.

(4) H. M. McConnell, *J. Chem. Phys.*, **33**, 115 (1960); *ibid.*, **33**, 1868 (1960).

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NOBORU HIROTA
S. I. WEISSMAN

RECEIVED JULY 1, 1961

THE STEREOCHEMISTRY OF AN ETHYLENEDIAMINETETRAACETATO COMPLEX OF MANGANESE(II)¹

Sir:

In further elucidation of the frequently unorthodox stereochemistry^{2,3} of ethylenediaminetetraacetato (EDTA, Y⁻⁴) chelates, we have utilized spectrometrically measured X-ray diffraction data from the acid salt, Mn[Mn(OH₂)HY]₂·8H₂O, to give the remarkable structural features noted below. The monoclinic cell containing 2Mn[Mn(OH₂)HY]₂·8H₂O has $a = 9.21$, $b = 16.10$, $c = 11.88 \text{ \AA}$, $\beta = 90.60^\circ$; the space group is P2₁/n. Intensity counts were taken with MoK α radiation for all forms $\{hkl\}$ in the range, $0 < (\sin \theta)/\lambda < 0.96$. Results given herein are based upon the data for $(\sin \theta)/\lambda < 0.67$, comprising 4440 forms of which 90% are recordable above background. Objective analysis by Patterson and Fourier methods, with subsequent partial refinement by difference syntheses, yield structural configurations with rather accurate bond parameters. Thermal parameters range from 1.50 Å^2 for manganese in the anion to above 3 Å^2 for oxygen in some water molecules. The discrepancy index for all 4440 forms is 0.10.

Manganous ions in fourfold positions of P2₁/n are centered in sexadentate seven-coördinate aquo complexes, [Mn(OH₂)HY]⁻. The geometry of the inner coördination group is not that reported³ for [Fe(OH₂)Y]⁻, but is roughly that of the sterically superior NbF₇⁼ configuration^{2,4} (*cf.* ref. 4 for diagram). Bond lengths, to the nearest 0.005 Å , are Mn-O, 2.210-2.260 Å , average of five, 2.235 Å ; Mn-N, 2.350, 2.395 Å . Apart from those angles and bonds which involve the central atoms, the geometry of ring systems is very like that expected from earlier studies^{5,6} of CoY⁻ and Ni(OH₂)H₂Y. Manganous ions in twofold ($\bar{1}$) positions of P2₁/n display octahedral coördination; each such ion is bonded to four water molecules and two not otherwise complexed oxygen

(1) Part of a program supported by the National Science Foundation. We thank also the U. S. Army Research Office (Durham) and the Advanced Research Projects Agency for support of the work reported herein.

(2) *Cf.* J. L. Hoard, G. S. Smith and M. Lind in "Advances in the Chemistry of Coördination Compounds," C. Stanley Kirschner, The Macmillan Company, New York, N. Y., July, 1961.

(3) J. L. Hoard, M. Lind and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961).

(4) J. L. Hoard, *ibid.*, **61**, 1252 (1939).

(5) H. A. Weakliem and J. L. Hoard, *ibid.*, **81**, 549 (1959).

(6) Gordon S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959).