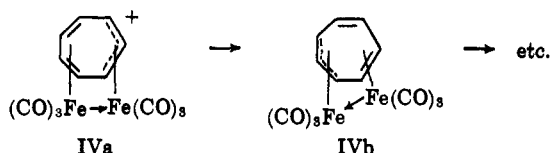


and the fluoroborate salt of a $C_7H_7Fe_2(CO)_6$ cation.⁶ This same salt is also obtained from the methoxy complex (III, R = OCH₃) upon reaction with HBF₄. The complex salt reacts with NaBH₄ to regenerate cycloheptatriene-Fe₂(CO)₆ (III, R = H); the p*K*_R⁺ value of 8.0 indicates that it is considerably more stable than the $C_7H_7Fe(CO)_3$ cation reported in the preceding paper, but the most interesting feature of this complex cation is that it displays only one sharp single n.m.r. absorption which occurs at 5.2 τ .

We suggest that the structure of this complex cation is as shown in IVa where it is implied that the C_7H_7 ring is bonded to one iron atom as in a diene-Fe(CO)₃ complex⁷ and to the other iron atom through the remaining three carbons as in the known π -allyl-Fe(CO)₃ cations.⁸ An Fe→Fe dative bond preserves the inert gas structure of each iron.



In order to account for the single n.m.r. absorption it is proposed that in solution rapid valence tautomerism to the equivalent structure (IVb) occurs with interchange of the roles of the two iron atoms. Such valence tautomerism would involve a rotation of $\pi/7$ of the Fe-Fe bond about the center of the ring. Seven such rapid interchanges would then result in equivalence of the seven protons in the n.m.r. spectrum.⁹

Acknowledgment.—We thank the National Science Foundation and the Robert A. Welch Foundation for financial assistance. We also thank Antara Chemicals for a gift of iron carbonyl.

(6) This salt crystallizes in orange needles from nitromethane; m.p. 170° dec.

(7) R. Pettit and G. F. Emerson, "Advances in Organometallic Chemistry," F. G. A. Stone and R. West, Eds., Academic Press, New York, N. Y., 1964, pp. 1-46.

(8) G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962); G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind. (London)*, 836 (1964).

(9) It is interesting that if one assumes values of 4.8 and 7.0 τ for the chemical shifts of the internal and terminal protons of a cyclic diene-Fe(CO)₃ species⁷ and values of 4.8 and 4.5 τ for the terminal and central protons of a π -allyl-Fe(CO)₃ fragment,⁸ then the average of these is 5.4 τ which is reasonable agreement with the observed value of 5.2 τ for IV.

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RECEIVED JULY 6, 1964

On Variations in the Hyperfine Splitting of Benzene Negative Ion and on the Value of Q^1

Sir:

A prime source of the value of Q in the equation $a = Q\rho$, proposed by McConnell² and describing the proton

(1) Supported in part by the U. S. Atomic Energy Commission.

(2) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956); **24**, 764 (1956).

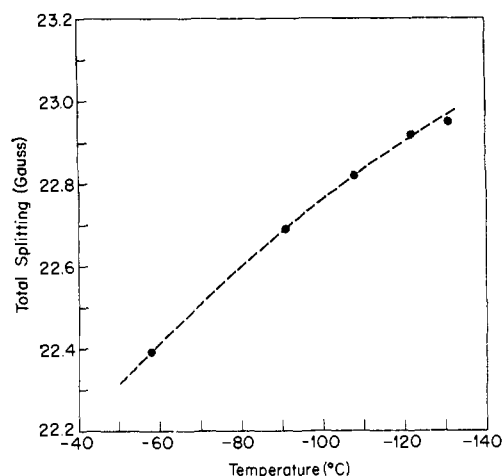


Fig. 1.—Total spread of the seven lines of the e.s.r. spectrum of benzene negative ion as a function of temperature; the ion was produced by reduction with sodium-potassium alloy in a 2:1 mixture of 1,2-dimethoxyethane and tetrahydrofuran.

hyperfine splitting, a , by a proton bonded to a carbon atom with a π spin density, ρ , is the total spread of the e.s.r. spectrum of the benzene negative ion. This species is particularly important because, in contrast to other aromatic ion radicals, it has a hydrogen attached to each carbon of the π -electron system and therefore a probe of the spin density at each position. In addition, this radical has the trigonal 120° bond angles.³ When the equation was first proposed,² the suggested value for $|Q|$ was the total spread of the spectrum of benzene negative ion. The value originally reported⁴ seems also to have been found by later workers.⁵ The purpose of this communication is to present some data which demonstrate a temperature dependence for the total spread of this spectrum and to try to relate this value to the value for Q from some other systems.

The benzene negative ion was produced by reduction of benzene by sodium-potassium alloy in a 2:1 mixture of 1,2-dimethoxyethane and tetrahydrofuran.⁵ The sample was cooled by cold nitrogen flowing through a dewar tube surrounding the sample. A thermal junction wedged between the sample tube and the wall of the dewar tube was used to measure and control sample temperature. Measurements with a second thermocouple placed in a sample tube filled with pentane showed that the sample temperature was known to about 2°. The e.s.r. spectrometer was a Varian unit with 100 kc./sec. field modulation and used a Varian 12-in. magnet. The field and microwave frequency measuring equipment was described previously.⁶

The total spread of the spectrum as a function of temperature is shown in Fig. 1. These data are the results of several different runs. Experiments were also done with sodium alone and with a solvent mixture much richer in tetrahydrofuran. Points for these runs seemed to fall ≈ 0.05 gauss below the curve of Fig. 1, but it is not clear that a significant difference exists so these points are not shown. The line width was about 0.6-0.8 gauss and no attempt was made to narrow it

(3) Neglecting any instantaneous distortions arising from the Jahn-Teller effect.

(4) T. R. Tuttle and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958).

(5) J. R. Bolton, *Mol. Phys.*, **6**, 219 (1963).

(6) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

further. The estimated error in a splitting measurement is about ± 0.02 gauss or less.

Temperature dependences of splittings have been reported for anion radicals such as that of toluene,⁷ but here an explanation involving the change in mixing of the two nearly degenerate electronic levels seems appropriate. Solvent dependences of splittings in unsubstituted aromatic ions⁸ have been found, but these seem, in part at least, to be of a compensating nature corresponding to varying distributions of spin density in the π -system. The case of benzene is simpler in that all positions have attached hydrogens, and a change in the over-all spread corresponds clearly to a change in Q . If the systems containing benzene are like those with higher aromatics,⁹ then the Q value for the free ion is represented by some value obtained by extrapolating the curve of Fig. 1 to lower temperatures. A larger value of the total splitting would fit in better with the Q values obtained from other radicals.

The other known systems which measure Q directly are the cyclooctatetraene anion radical and the cyclo-C₅H₅ and cyclo-C₇H₇ radicals. Values for these radicals are given in Table I. Allyl and cyclohexadienyl radi-

reported here is the first one determined in the liquid phase. Our value for the total splitting of cyclo-C₇H₇ in hydrocarbon solvents is in excellent agreement with that found by Carrington and Smith for water solvent in a flow experiment.

It should be pointed out that the line widths found in our experiments for both cyclo-C₅H₅ (<0.5 gauss) and cyclo-C₇H₇ (0.2 gauss) are similar to or only slightly larger than those (cyclo-C₇H₇) for more usual hydrocarbon radicals⁶ without orbital degeneracy. This fact leads to the suggestion that, in the experiment of Santos-Veiga who used sodium-potassium alloy to reduce tropylium bromide, the large line width of 2.88 gauss for cyclo-C₇H₇ radical arose because the radicals were produced on the metal surface and were not truly in solution.

The values given in Table I vary more than might be hoped. The cyclo-C₅H₅ and cyclo-C₇H₇ pair show splittings which differ in the manner predicted by considerations of the changes in hybridization,¹⁰ but both of these values are larger than values derived from neutral radicals such as allyl and cyclohexadienyl with closer to 120° geometry. Unless the splitting for benzene negative ion could be extrapolated to much higher values, no similar behavior of the C₆H₆⁻ and C₈H₈⁻ pair would occur. The dependence of splitting upon excess charge density¹¹ is not strong enough to invert this pair. In defense of the neglect of the Jahn-Teller effect in comparing Q values can be stated the fact that the sum of the splittings at the 2, 3, 5, and 6 positions plus twice that at the 4 position of benzene-1-*d* anion equals 1.000 \pm 0.001 times the total spread of the spectrum of the unsubstituted species.¹²

In conclusion, it can be said that, although some possibility of a larger value for the total splitting of the spectrum of a free benzene negative ion has been established, there is no indication of how much larger the true value may be. With a firm liquid-phase value for the total splitting of the spectrum of cyclo-C₅H₅ radical, it becomes increasingly clear that no treatment presented so far can explain in detail the differences between the Q values derived from these different radicals.

(10) I. Bernal, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, **1489** (1962).

(11) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

(12) R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and T. H. Brown, *J. Am. Chem. Soc.*, **86**, 520 (1964).

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RECEIVED JUNE 26, 1964

Stereochemical Identification and Synthesis of Amicetose and the Stereochemical Identification of Rhodnose and the Sugar from Streptolydigin

Sir:

The 2,3,6-trideoxyaldohexose I has been shown to be a component of the antibiotics amicetin,¹ rhodomycin,² and streptolydigin.³ In the work reported here amicetose, the component of amicetin, was shown to be 2,3,6-

(1) C. L. Stevens, K. Nagarajan, and T. H. Haskell, *J. Org. Chem.*, **27**, 2991 (1962).

(2) H. Brockmann and T. Waehneltd, *Naturwiss.*, **50**, 43 (1963).

(3) K. L. Rinehart, Jr. and D. B. Borders, *J. Am. Chem. Soc.*, **85**, 4037 (1963).

TABLE I

TOTAL SPREAD OF THE E.S.R. SPECTRA OF VARIOUS CYCLIC RADICALS

Radical	Total splitting, gauss	Phase	Ref.
C ₅ H ₅	28.0	Solid	<i>a</i>
	29.9	Solid	<i>b</i>
	30.00 \pm 0.05	Liquid	<i>c</i>
C ₆ H ₆ ⁻	22.95	Liquid	<i>d</i>
	27	Solid	<i>e</i>
C ₇ H ₇	27	Solid	<i>f</i>
	25.6	Liquid?	<i>g</i>
	27.4 \pm 0.14	Liquid	<i>h</i>
	27.67 \pm 0.05	Liquid	<i>i</i>
	25.67 \pm 0.07	Liquid	<i>c</i>

^a S. Ohnishi and I. Nitta, *J. Chem. Phys.*, **39**, 2848 (1963).

^b P. J. Zandstra, *ibid.*, **40**, 612 (1964). ^c This work. Radicals were produced by irradiation of hydrocarbons or hydrocarbon mixtures in steady-state experiments similar to those previously described.⁶ Temperatures were in the range -50 to -90°. Slight ($\sim 1\%$) solvent dependences have been noted. ^d This work. This value is at about -130°. ^e D. E. Wood and H. M. McConnell, *J. Chem. Phys.*, **37**, 1150 (1962). ^f S. Arai, S. Shida, K. Yamazaki, and Z. Kuri, *ibid.*, **37**, 1885 (1962). ^g J. dos Santos-Veiga, *Mol. Phys.*, **5**, 639 (1962); see text. ^h A. Carrington and I. C. P. Smith, *Mol. Phys.*, **7**, 98 (1963-1964). ⁱ T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960).

cals also can be used to measure Q since all positions have attached hydrogens, but here it must be assumed that Q is the same for all positions, including those of negative spin density. The values derived in this way for these two systems, -24.7 and -25.7 gauss, respectively,⁶ are nevertheless in better agreement with those for cyclic systems than is the value for benzene negative ion, especially if no account is taken of the temperature dependence.

It should be noted that there are included in Table I splittings determined in this laboratory for cyclo-C₅H₅ and cyclo-C₇H₇ radicals. The value for cyclo-C₅H₅

(7) T. R. Tuttle, *J. Am. Chem. Soc.*, **84**, 1492 (1962).

(8) See, for example, the results on biphenyl anion radical: H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi, and H. Takaki, *J. Chem. Phys.*, **40**, 241 (1964).

(9) There is usually increased dissociation of the ion pair at lower temperatures because of the increased dielectric constant of the solvent: A. C. Aten, J. Dieleman, and B. J. Hoijtink, *Discussions Faraday Soc.*, **29**, 182 (1960).