at 474 Hz (the same as in thyroxine) and the 2′,6′, and 5′ protons as a multiplet centered around 415 Hz. The addition of $CuCl_2$ results in a broadening of all signals and although the 2,6 signals were most affected, this may not be due to the Cu^{2+}–iodine interaction as much as the proximity of C_2H and C_6H to the "glycine-like" bonding site, which is the amino nitrogen and the carboxyl oxygen.

Table I gives the half-width in Hz of nmr proton signals for tyrosine and its analogs (0.2 *M* in D_2O, pD ~12), as a function of $CuCl_2$ concentration. It is seen that the broadening effect of copper(II) on the C_2–(C_2–(C_6)H and on the C_3–(C_5)CH_3 signals is greater for 3,5-dimethyltyrosine that for 4-methoxy-3,5-dimethyltyrosine. This can only be explained if there is some interaction between the oxygen atom on C_4 and the Cu^{2+} ion. The large broadening effect of Cu^{2+} ion on the C_2–(C_6)H of 3,5-diiodotyrosine, compared with the C_2–(C_6)H of tyrosine analogs which contain no iodine atom, can be explained by the interaction between iodine and the copper(II) ion.

Table I. Half-Width of Proton Signals for Tyrosine and Its Analogs (0.2 *M* in D_2O, pD ~12), as Function of $CuCl_2$ Concentration

		—[$CuCl_2$] × 10^4, *M*—			
		0	1.0	3.0	5.0
	Group	Half-width, Hz			
3,5-Diiodotyrosine	C_2–(C_6)H	1.5	2.4	4.6	7.0
3,5-Dimethyltyrosine	C_2–(C_6)H	2.6	3.0	3.6	5.5
4-Methoxy-3,5-dimethyltyrosine	C_2–(C_6)H	2.8	3.2	3.5	4.6
3,5-Dimethyltyrosine	CH_3	2.0	2.1	2.9	3.8
4-Methoxy-3,5-dimethyltyrosine	CH_3	1.7	1.9	2.0	2.6
4-Methoxy-3,5-dimethyltyrosine	OCH_3	1.2	1.3	1.5	1.6

Zand and Palmer[4] have shown that copper(II) complexes of iodinated amino acids in DMSO have λ_{max} at 610 nm (ϵ ~80) and also possess a charge-transfer band between 330–410 nm (ϵ 15–1500). Noniodinated amino acids exhibit no absorption in the near uv because the charge-transfer band is missing. Copper(II) complexes of the three iodinated amino acids, thyroxine, 3,5-diiodothryonine and 3,5,3′-triiodothyronine, all possess similar spectra. Our spectral data in Table II agree with those of Zand and Palmer.

Table II. Electronic Spectral Data for DMSO Solutions Containing 0.02 *M* $Cu(ClO_4)_2 \cdot 6H_2O$

			Charge-transfer band	
0.1 *M*	λ_{max}, nm	ϵ	λ_{max}, nm	ϵ
Thyroxine	610	77	330	1550
3,5-Diiodothyronine	610	80	380	115
3,5,3′-Triiodothyronine	610	80	380	35
3,5-Diiodotyrosine	610	77	410	14

If the intensity of the charge-transfer band can be taken as a criterion of the copper–iodine interaction, it would appear that this is a maximum in thyroxine and a minimum in 3,5-diiodotyrosine. This strongly indicates that structure III, as postulated by Zand and Palmer,[4] is the most probable.

The claim[4] that the stoichiometry of copper(II)–thyroxine complexes is the same in DMSO as in water is supported by data from Laurie.[7] He showed that isomeric copper(II)–tyrosine complexes all gave identical spectra in water, pyridine, DMSO, and *N,N*-dimethylformamides.

It appears from the present study that nmr selective line broadening of signals by paramagnetic copper(II) and electronic spectral data do afford evidence for some sort of interaction between an iodine atom of thyroxine and analogs, and the copper to which these molecules are bound. It is suggested that the iodine atom interacts with the square-planar copper(II) ion that assumes square-pyramidal 5-coordination.

(7) S. H. Laurie, *Aust. J. Chem.*, **20**, 2615 (1967).

Communications to the Editor

Unsubstituted Cyclopentadienyl Cation, a Ground-State Triplet

Sir:

There has recently been considerable interest in such antiaromatic 4π-electron species as the cyclopropenyl anion, cyclobutadiene, and the cyclopentadienyl cation. Attention has focused not only on the energy of these species, but also on their electronic and geometric structures. In particular, these substances and any derivatives of them which retain their *n*-fold symmetry are predicted to be possible ground-state triplet, rather than normal singlet, molecules. In the case of cyclopentadienyl cation, our PPP-SCF calculations[1] indicate that the symmetrical triplet should be 0.318 eV more stable than the completely symmetrical singlet state. Of course, this 7.3 kcal/mol energy advantage must be balanced against the stabilization that the symmetrical singlet could gain by undergoing Jahn–Teller distortion, either to a somewhat less symmetrical planar structure[2] or perhaps even to more extreme geometries.[3]

A certain amount of evidence about this system is available. Thus, pentaphenylcyclopentadienyl cation[4,5] is a ground-state singlet whose triplet state lies approximately 1 kcal/mol higher. A number of other pentaarylcyclopentadienyl cations have also been

(1) Using standard values for integrals and all singly excited configurations. The S–T gap without configuration interaction is calculated to be 0.470 eV.

(2) L. Snyder (*J. Phys. Chem.*, **66**, 2299 (1962)) predicts that Jahn–Teller distortion to C_{2v} symmetry would stabilize the singlet by 5.25 kcal/mol.

(3) W.-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

(4) R. Breslow, H. W. Chang, and W. A. Yager, *ibid.*, **85**, 2033 (1963).

(5) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *ibid.*, **89**, 1112 (1967). The conversion factor on p 1114 should be 0.09348 cm^{-1} = 1000 G.

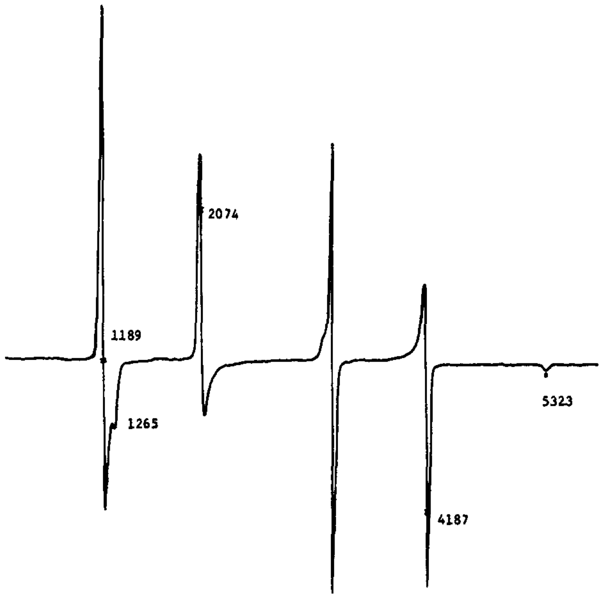
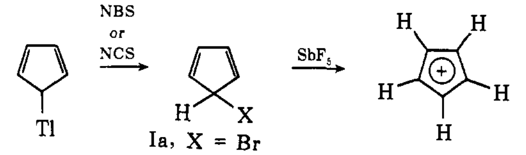


Figure 1. The epr spectrum of $C_5H_5^+$ at 78°K in a matrix of SbF_5.

studied,[5–7] in all of which the ground state is a singlet. However, when hexachlorocyclopentadiene is treated with SbF_5 it is converted to pentachlorocyclopentadienyl cation, which is in fact a ground-state triplet.[5,8] From this it was reasonable to expect that the unsubstituted cyclopentadienyl cation, if it could be prepared, would also be a ground-state triplet species.

Methods have recently become available for preparing 5-iodocyclopentadiene,[9] 5-bromocyclopentadiene,[10] and 5-chlorocyclopentadiene.[10] These are attractive precursors of unsubstituted cyclopentadienyl cation, although they do not afford this cation under mild solvolytic conditions.[9] We now wish to report that 5-bromocyclopentadiene (Ia) can be converted to the unsubstituted cyclopentadienyl cation II on treatment with SbF_5, and that this cation is indeed a triplet.



Ia, X = Br
b, X = Cl

II

Solutions of the 5-bromo- or 5-chlorocyclopentadienes (I) are prepared by treatment of thallium cyclopentadienide with the *N*-halosuccinimide in various solvents. The products (I) are identified both from the Diels–Alder dimers they form on warming the solutions and from their adducts with *N*-phenyltriazolinedione. To prepare the cation II, Ia (*ca.* 1 mmol) was prepared in di-*n*-butyl phthalate and vacuum transferred into one side of a molecular beam reaction apparatus.[11] Concurrently, 2 g (9 mmol) of SbF_5 was transferred from a bulb on the other side of this apparatus into the reaction chamber held at 78°K. When the transfer was complete a magnetic stirring bar was used to powder the product and it was transferred as a solid at 78°K into an epr tube.

The epr spectrum (Figure 1) of the product at 78°K showed triplet signals at 1189 ± 5, 1265, 2074 ± 2, 4187 ± 2, and 5323 ± 2 G. (A line at 3283 G (g = 2.010) is assigned to monoradical impurities.) The g_{xy} value is 2.0023 ± 0.0011 and the D value is calculated[12] to be 0.1868 ± 0.0005 cm^{-1}. The same (but weaker) spectrum was obtained from 5-chlorocyclopentadiene (Ib). In addition, the triplet spectrum[5,8] of $C_5Cl_5^+$ was observed in this latter case, apparently from contamination of Ib with hexachlorocyclopentadiene.

Figure 1 is certainly the epr spectrum of the triplet state of II. The coincidence of the x and y lines ($E < 0.001$, indicating plane regular polygonal symmetry) and the weakness of the z line are expected for II and are consistent with results[5,8] for the $C_5Cl_5^+$ triplet. The value of D for II is somewhat larger than the 0.1495-cm^{-1} value for $C_5Cl_5^+$, as expected since II is less delocalized. Curie law studies indicate that II, like $C_5Cl_5^+$, is in fact a ground-state triplet.[13] Thus, one of the most significant predictions of molecular quantum mechanics for $C_5H_5^+$, the cyclopentadienyl cation, has been confirmed.

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(6) W. Broser, H. Kurreck, and P. Siegle, *Chem. Ber.*, **100**, 788 (1967).

(7) W. Braser, P. Siegle, and H. Kurreck, *ibid.*, **101**, 69 (1968).

(8) R. Breslow, R. Hill, and E. Wasserman, *J. Amer. Chem. Soc.*, **86**, 5349 (1964).

(9) R. Breslow and J. M. Hoffman, Jr., *ibid.*, **94**, 2110 (1972).

(10) Reported by R. Breslow and J. Hoffman, Jr., at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

(11) M. Saunders and D. Cox, *J. Amer. Chem. Soc.*, submitted for publication.

(12) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1954).

(13) Good Curie law behavior was observed for most samples down to liquid helium temperature. Although some showed deviations near 10°K, this was related to the prior history of the sample.

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A Molecular Beam Method for Preparing Carbonium Ion Solutions

Sir:

Through addition of solutions of alkyl halides to solutions of SbF_5 at low temperature, it has been possible to prepare stable solutions of many simple organic cations.[1,2] We have encountered two circumstances where this procedure is limited. Ions which can readily rearrange to isomers are difficult to obtain pure. The reaction of halides with SbF_5 is strongly exothermic; hence the heat released on the addition of each drop of reactant raises the temperature locally. Thus, *sec*-butyl cation which rearranges rapidly to *tert*-butyl cation only at −30° was always obtained rearranged to the extent of at least 25% even when the preparation was performed slowly using a dilute solution of the halide at a *bath temperature* of −120°.

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(1) G. A. Olah and M. Comissarow, *J. Amer. Chem. Soc.*, **88**, 1818 (1966).

(2) M. Saunders and E. L. Hagen, *ibid.*, **90**, 2436 (1968).