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Studies of Phenylxanthyl and Its Analogues by Electron Spin Resonance

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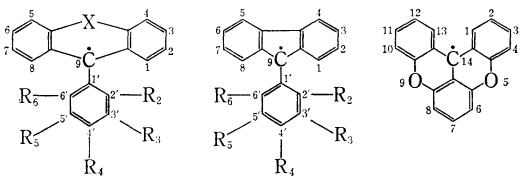
Phenylxanthyl, phenylthioxanthyl, phenylselenoxanthyl, 9-phenylfluorenyl, dioxadehydrocoranthryl, and their derivatives were studied by the electron spin resonance (ESR) technique, and the odd-electron distribution in the radicals was examined. From the results, the angle between the plane of the phenyl group and the plane of the rest of the molecule was estimated at about 63°. Since these radicals are in equilibria with their dimers, heat of reaction in the system was also determined on two of them. Some discussion of the correlation between the heat of reaction and the molecular shape was undertaken.

The distribution of the odd-electron in a molecule can be determined directly by the ESR technique. In this study, phenylxanthyl and its analogues, I—XI, were examined by this method. Since, in their structural features, these radicals have a form in which two or three phenyl groups of triphenylmethyl are bridged, the investigation of these radicals is interesting, especially in the correlation between the structure and the odd-electron distribution.



I—VIII IX—X XI

I, X=O, $R_2=R_3=R_4=R_5=R_6=H$
II, X=O, $R_2=R_3=R_5=R_6=H$, $R_4=OCH_3$
III, X=O, $R_3=R_4=R_5=R_6=H$, $R_2=OCH_3$
IV, X=S, $R_2=R_3=R_4=R_5=R_6=H$
V, X=S, $R_2=R_3=R_5=R_6=H$, $R_4=OCH_3$
VI, X=SO_2, $R_2=R_3=R_4=R_5=R_6=H$
VII, X=Se, $R_2=R_3=R_4=R_5=R_6=H$
VIII, X=O, $R_2=R_3=R_4=R_5=R_6=D$
IX, $R_2=R_3=R_4=R_5=R_6=H$
X, $R_2=R_3=H$, $R_2=R_4=R_6=CH_3$

Results and Discussion

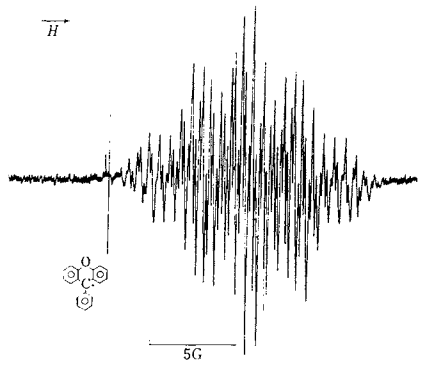
All the radicals examined here were produced in a vacuum-sealed sample tube by treating the corresponding chlorides dissolved in a suitable solvent with amalgamated silver. The ESR measurements were made at room temperature in solutions, using THF as the solvent except in the cases of compounds IX and X. Since these compounds are scarcely dissociated to the radical form at room temperature, their ESR measurements were conducted at an elevated temperature (80°C) using xylene as the solvent.

The proton hyperfine coupling constants obtained by the analyses of the ESR spectra are tabulated in Table 1. The coupling constant due to the proton was assigned tentatively by comparison with the spectra obtained from the measurements of non-substituted phenylxanthyl and the substituted phenylxanthyl derivatives, with reference to the results of the HMO calculations. Finally, such assignments were substantiated by comparison with the ESR spectrum of d_5-phenylxanthyl. Since phenylthio- and phenylseleno-xanthyl have shown spectra quite similar to that of phenylxanthyl, as can be seen in Fig. 1, the assignments of the corresponding protons to the respective coupling constants were straightforward. As to the other compounds (IX, X, and XI), the analyses of the spectra

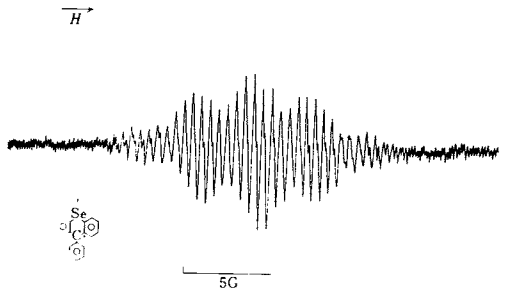
TABLE 1. PROTON HYPERFINE COUPLING CONSTANTS OF RADICALS (gauss)

Radical \ a_H position	1,8	2,7	3,6	4,5	2′,6′	3′,5′	4′
I	2.65	0.60	2.60	0.64	0.55	0.91	0.55
II	2.86	0.64	2.86	0.64	0.64	0.20	
III	3.76		3.76				
IV	3.28	0.47	3.10	0.47	0.95		1.16
V	4.15	0.57	4.15	0.57	1.13		
VI	3.63	0.48	3.55	0.48	0.96		1.25
VII	3.70	0.59	3.70	0.59	1.17		1.17
VIII	2.65	0.60	2.60	0.64			
IX	3.28	0.58	3.47	0.97	1.95	0.39	1.95
X	3.77		3.77				

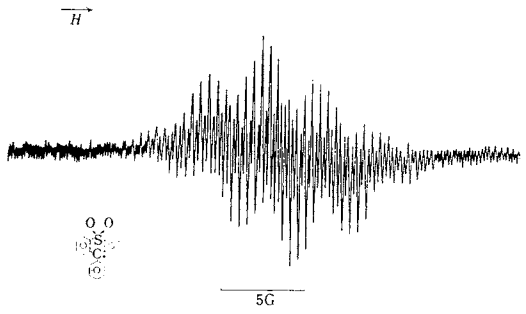
Radical \ a_H position	1,13	2,12	3,11	4,10	6,8	7
XI	2.77	0.84	2.97	0.84	0.65	2.97



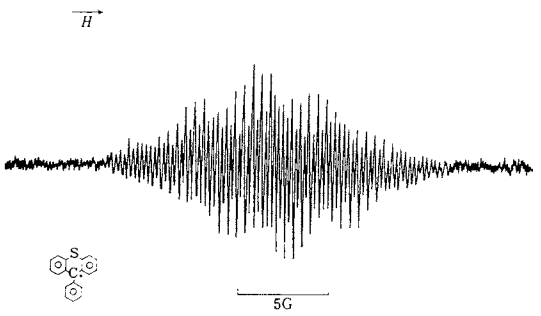
(a) ESR spectrum of I



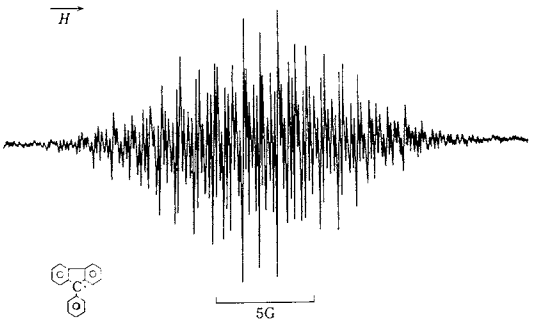
(b) ESR spectrum of III



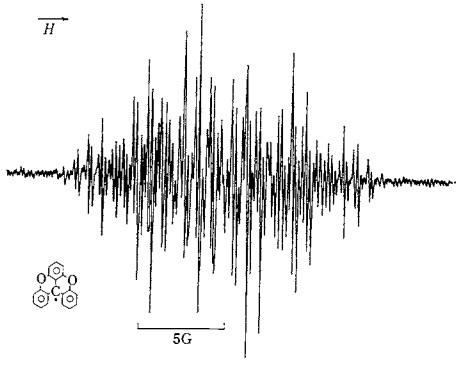
(c) ESR spectrum of VI



(d) ESR spectrum of VII



(e) ESR spectrum of IX



(f) ESR spectrum of XI

Fig. 1. ESR spectra of phenylxanthyl and its analogues.

and the assignments of the proton coupling constants were made quite analogously. The coupling constants obtained from the analyses of the spectra were reconfirmed by simulation with a computer.

It is interesting to compare the proton hyperfine coupling constants of these phenylxanthyl derivatives with that of triphenylmethyl, in which there is no bridge connecting the two phenyl groups. The proton hyperfine coupling constants of triphenylmethyl have been measured by several investigators. The values of the coupling constants for the respective protons reported by Ayscough and his co-workers[1] are $a_{\mathrm{H}ortho}$: 2.55 gauss, $a_{\mathrm{H}para}$: 2.78 gauss and $a_{\mathrm{H}meta}$: 1.11 gauss. Although the value of the coupling constant can be slightly affected by the species of solvent used, those of the phenyl protons of phenylxanthyl as well as of the thio- or seleno-derivatives are outstandingly reduced compared with those of the corresponding protons of triphenylmethyl. This indicates the smaller delocalization of the odd-electron on the phenyl group. This may be due to the $C_{1'}$–C_9 bond twist of phenylxanthyl and its analogues. In view of the molecular model, the $C_{1'}$–C_9 bond of phenylxanthyl can be said to be forced to twist strongly because of the repulsion which might operate among C_1–H, C_8–H, $C_{2'}$–H, and $C_{6'}$–H. The results of HMO calculations performed under the consideration of the $C_{1'}$–C_9 bond twist are

1) P. Ayscough, A. McCann and R. Wilson, *Proc. Chem. Soc.*, **1961**, 16; D. Chesnut and G. Sloan, *J. Chem. Phys.*, **33**, 637 (1960).

TABLE 2. HMO CALCULATION OF ODD ELECTRON DENSITY OF PHENYLXANTHYL*

Angle of deviation** (in degree)	0	10	20	30	40	50	60	70	80	90
c_1***	.07371	.07426	.07585	.07846	.08191	.08602	.09036	.09419	.09691	.09791
c_3	.06632	.06729	.06864	.07086	.07382	.07728	.08094	.08422	.08649	.08732
c_9	.27100	.27280	.27820	.28680	.29820	.31150	.32540	.33760	.34620	.34930
$c_{4'}$	.07629	.07458	.06943	.06116	.05009	.03717	.02369	.01160	.00308	.00000

* The values; α_0: $\alpha+1.3\beta$, β_{C-O}: 1.5β are used for the calculation.
** Angle of deviation from the co-planar position.
*** c_1, c_3, c_9 and $c_{4'}$ are coefficients of the corresponding atomic orbitals in a molecular orbital where odd electron is found.

shown in Table 2.

The variation in the value of $(c_{4'}/c_1)^2$ with the value of the twisted angle is figured in Fig. 2, where $(c_1)^2$ and $(c_{4'})^2$ represent the odd-electron density on the respective carbon atoms (C_1 and $C_{4'}$).

By a comparison of the ratio of the coupling constants ($a_{H4'}/a_{H_1}$) experimentally obtained with the value in Fig. 2, the angle of twist of the $C_{1'}$–C_9 bond can be estimated to be about 63° for phenylxanthyl. Therefore, it may be assumed that there is a comparable order of $C_{1'}$–C_9 bond twist for thio- or selenoxanthyl derivatives, too. Such a situation is partly reflected in the equilibrium between a radical and the dimer. The relative stability of phenylxanthyl and of 9-phenylfluorenyl in comparison with that of the dimers was determined by the ESR technique (see Fig. 3). The values obtained are tabulated in Table 3, along with those of other compounds.

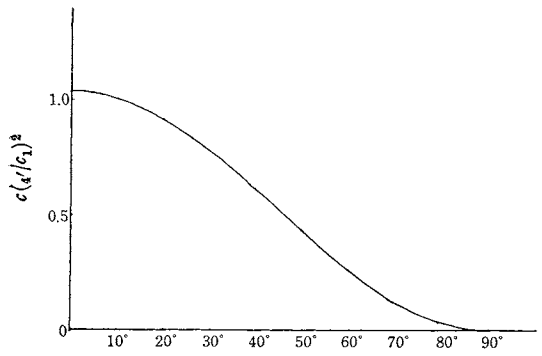


Fig. 2. Relation between $(c_4'/c_1)^2$ and angle of deviation from the co-planar position.

Since the degree of dissociation of a dimer to the radical is determined simply by the relative stability between the dimer and the resulting radical, the degree of dissociation must be controlled by two main factors. One is the stabilization of the radical due to the delocalization of the odd-electron, while the other is the steric repulsion around the bond-forming center (the central carbon atom) to

TABLE 3. HEAT OF REACTION (ΔH) IN THE SYSTEM OF EQUILIBRIUM BETWEEN RADICAL AND THE DIMER

Compound	ΔH (kcal/mol)
Phenylxanthyl dimer	8.4
9-Phenylfluorenyl dimer	26.6
Hexaphenylethane*	18.2
Pentaphenylethane*	27.0

* J. Leffler, "The Reactive Intermediate of Oragnic Chemistry," Florida University Press (1956).

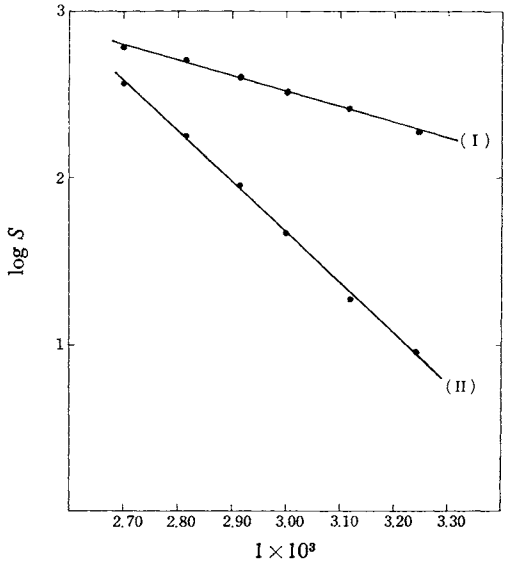


Fig. 3. Temperature dependence of radical concentration (S: signal intensity).
(I) phenylxanthyl (II) 9-phenylfluorenyl

dimerize. The former causes the potential energy of radical to be lower, while the latter causes that of its dimer to be higher. The latter is the predominant factor in the dissociation of hexaphenylethane derivatives to triphenylmethyls.[2] Therefore, the lower heat of reaction in the system

2) W. Theilacker, H. Schultz, U. Baumgarte, H.-G. Prossler, W. Rohde, F. Thater and H. Uffmann, *Angew. Chem.*, **69**, 322 (1957).

of the equilibrium between phenylxanthyl and its dimer compared with that in the cases of triphenylmethyl and 9-phenylfluorenyl can be reasonably concluded to be the result of the larger steric repulsion around the central carbon atom due to the phenyl group being situated nearly perpendicular to the rest of the molecule. The larger value of the coupling constants (1.95 gauss) due to 2′,4′,6′-protons of 9-phenylfluorenyl compared with the value of the coupling constants (0.55 gauss) of the 2′,4′,6′-protons of phenylxanthyl may be considered to be a direct reflection of the more favorable situation for the co-planarity of phenyl and fluorenyl groups in IX because of the less repulsive force between C_1–H, C_8–H, $C_{2'}$–H, and $C_{6'}$–H. Moreover, it is consistent with the higher heat of reaction in the system. The larger coupling constant (2.97 gauss) of the 3,7,11-protons of dioxadehydrocoranthryl (XI), in which three phenyl groups are forced to be co-planar, supports the above discussion.

Experimental

Materials. All the free radicals examined were made *in situ* by shaking their chlorides with amalgamated silver in a vacuum cell, and the ESR spectra were immediately observed. The chlorides were prepared from the corresponding alcohols by treatment with gaseous hydrogen chloride in ether. The method of synthesizing chlorides and their physical constants are shown in Table 4.

The ESR spectra were measured by means of a 3BX-type spectrometer manufactured by the Japan Electron Optics Lab.

Determination of the Heat of Reaction. A known amount of chloride was dissolved into a known amount of tetrahydrofuran in a cell suitable for ESR measurements, and then it was evacuated and treated with amalgamated silver which had previously been prepared in the cell. The signal intensity was measured at various temperatures according to the usual way (magnetic field modulation: 5 gauss). The $\ln S$(S: signal intensity) *vs.* $1/T$ plot gave directly the heat of reaction in the system of equilibrium. A DPPH solution dissolved in THF of a known concentration was used as the standard solution.

Table 4. Synthetic methods of chlorides and their physical constants

Precursor of*	Synthetic method	Melting point of alcohol (°C)	Melting point of chloride (°C)	Ref.
I	Xanthone $+C_6H_5MgBr$	158	106*	3
II	Xanthone $+p$-$CH_3OC_6H_4MgBr$	121	96**	4
III	Xanthone $+o$-$CH_3OC_6H_4MgBr$	oil	75—80**	
IV	Thioxanthone $+C_6H_5MgBr$	106	115**	5
V	Thioxanthone $+p$-$CH_3OC_6H_4MgBr$	135	87—90**	
VI	Sulfonylxanthone $+C_6H_5MgBr$	68	80—83**	
VII	Selenoxanthone $+C_6H_5MgBr$	115	134—136**	
VIII	Xanthone $+C_6D_5MgBr$	97	106—107**	
IX	Fluorenone $+C_6H_5MgBr$	107	78—80	6
X	Fluorenone $+2,4,6$-$(CH_3)_3C_6H_2Li$	oil	106—107	
XI	1-Hydroxyxanthone $+o$-$CH_3OC_6H_4MgBr$	180	243*)	7

* Precursors of radicals described in the column.
** Melting point of hydrolchloride of the corresponding chloride is shown.

The simulation of the ESR spectra was done by the Japan Electron Optics Lab., to the members of which our thanks are due.