Electron Spin Resonance Study of a Stable Benzo[*b*]furanyl Radical

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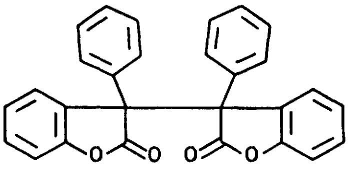
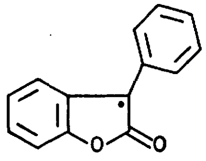
The structure of radicals of type (II) formed by the thermal decomposition of 2,2'-dioxo-3,3'-diphenyl-2,2',3,3'-tetrahydrobibenzo[*b*]furan-3-yl (I) has been studied. The approximate values of the coupling constants were determined using methyl or deuterium substitution and the e.s.r. spectra of (II) and some of its derivatives were computer-simulated. Spin densities were calculated by the INDO and McLachlan–Honeybourne methods. The calculated coupling constants were compared with those obtained by computer simulation.

THE benzo[*b*]furan ring is present in many naturally occurring oxygen-containing heterocycles. Information on free-radical reactions in this system is very limited and no e.s.r. study of the benzo[*b*]furanyl radical has been published so far.

The present work is devoted to a study of stable free radicals of type (II), with 2,2'-dioxo-3,3'-diphenyl-2,2',3,3'-tetrahydrobibenzo[*b*]furan-3-yl (DTDB) (I) as precursor. The structure of the latter suggests that the 3,3'-bond will be easily broken thermally due to steric hindrance. The radicals thus formed are expected to be stabilized by delocalization. Thus, *e.g.* a xylene solution of (I) becomes blue when heated to 70 °C. This colour disappears when the solution is cooled. The presence of stable free radicals has been verified by e.s.r. spectroscopy and the radicals formed were characterized.



(I)

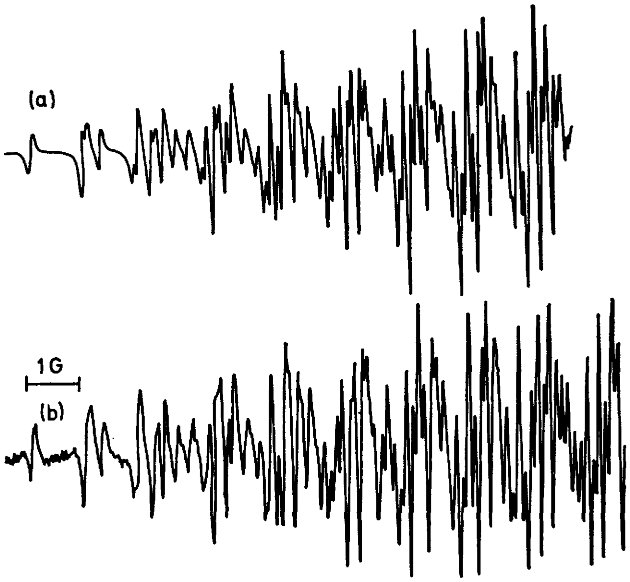


(II)

RESULTS

A degassed 0.05M solution of DTDB in xylene (10^{-5} Torr) in a sealed quartz tube (4 mm o.d.) was heated at 70 °C in the cavity of the e.s.r. spectrometer. The determination of hyperfine splitting constants was based on the well known substitution method.[1] For this purpose, we synthesized the 5,5'-dimethyl, 7,7'-dimethyl, 3,3'-di-*m*-tolyl, 3,3'-di-*p*-tolyl, 4,4',7,7'-tetramethyl, 5,5',6,6'-tetramethyl, 6,6',7,7'-tetramethyl, 6,6'-dimethyl-3,3'-di-*p*-tolyl, and 3,3'-di[$^2H_5$]phenyl analogues of (I). These derivatives were studied in the same manner as the parent compound (I).

The e.s.r. data are summarized in Table 1. From the total width of the e.s.r. spectra for each substituted methyl derivative, one can find the approximate values of the hyperfine splitting constants for radical (II). More accurate values can be obtained by the analysis of the extreme positions of the spectra (*cf.*, *e.g.*, Figure). Two additional pieces of information can be obtained from the e.s.r. spectrum of the 3,3'-di[$^2H_5$]phenyl derivative. (*a*) This radical has two large coupling constants, their values being between 3.5 and 5 G. (*b*) The sum of the hyperfine splitting constants of the 3-phenyl substituent is 9.61 G.



(a) Simulated and (b) experimental e.s.r. spectrum of radical (II) from 0.15M-DTDB at 80 °C

DISCUSSION

Computer Simulation of the E.s.r. Spectra and Accurate Determination of the Coupling Constants.—The e.s.r. spectra of the radicals derived from (I) and its 5,5'- and 6,6'-dimethyl and 3,3'-di-*p*-tolyl derivatives have been computer simulated. The other spectra were not simulated because, even under the best experimental conditions, their resolution is very poor and does not allow an accurate determination of hyperfine splitting constants. The coupling constants used for each simulation are given in Table 1. They have been determined with an accuracy of 0.01 G. Nevertheless, some slight differences remain in the central portion of the experimental spectra compared with the simulated ones. Since a 0.01 G variation of one of the coupling

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[1] L. Lunazzi, A. Mangini, G. F. Pedulli, and F. Taddei, *J. Chem. Soc.* (*B*), 1970, 163.

constants can result in significant differences in the central portion of the simulated spectrum the above mentioned differences can be regarded as an acceptable error.

Calculation of Spin Densities.—The assignment of the coupling constants to the different protons in (II) has been made by comparison of the spectra of the different methyl derivatives of (I). To confirm this assignment and to determine the sign of the coupling constants, we have calculated the spin densities of radical (II) by INDO [2] and McLachlan [3] methods.

TABLE 1

Compound	Total width (G)	X [a] (G)	$a_H^{CH_3}$ [b] (G)	Coupling constants (G) [c]						
				4	5	6	7	*ortho*	*meta*	*para*
DTDB (I)	20.42			3.69	1.05	4.67	1.31	2.51	0.97	2.74
5,5′-Dimethyl-DTBD	22.17	0.87	0.95	3.56		4.89	1.37	2.45	0.95	2.70
6,6′-Dimethyl DTDB	31.40	5.48	5.34	3.67	0.92		1.32	2.44	0.94	2.65
7,7′-Dimethyl-DTDB	23.27	1.42								
3,3′-Di[$^2H_5$]phenyl-DTDB	13.76									
3,3′-Di-*o*-tolyl-DTDB	22.00	0.78								
3,3′-Di-*p*-tolyl-DTDB	27.14	3.35	3.10	3.59	1.04	4.60	1.30	2.56	0.96	
4,4′,7,7′-Tetramethyl-DTDB	18.93 [d]									
5,5′,6,6′-Tetramethyl-DTDB	32.85									
6,6′,7,7′-Tetramethyl-DTDB	33.21	6.39								
6,6′-Dimethyl-3,3′-*p*-tolyl-DTDB	36.85	8.21								

[a] $X = 1/2$ difference between the total width of the spectrum studied and the width of the spectrum of radical (II). [b] $a_H^{CH_3}$ = hyperfine splitting constant of the methyl group determined by computer simulation. [c] Hyperfine splitting constants used for computer simulation. [d] A methyl group in the 4-position changes the angle θ between the planes of the phenyl ring and the benzo[*b*]furanyl system.

The geometry of radical (II) has been postulated on the basis of literature data. The molecular and crystal structure of benzo[*b*]furan has not been studied. We have used the geometry of the benzene ring for the 3-phenyl substituents and for the six-membered ring of the benzo[*b*]furan part of radical (II). Furan geometry has been used for the five-membered ring. We have taken 1.23 Å for the carbon–oxygen double bond of the carbonyl group and 1.5 Å for the C(3)-phenyl group bond length.

TABLE 2

Position	Experimental a_H/G	Theoretical a_H/G			
		INDO		McLachlan [a]	
		θ 0°	θ 37.5°	θ 0°	θ 37.5°
4	3.69	−3.45	−3.50	−3.57	−3.82
5	1.05	1.93	1.96	1.34	1.43
6	4.67	−3.17	−3.22	−3.04	−3.20
7	1.31	2.10	2.13	1.36	1.43
ortho	2.51	−3.40	−2.50	−2.25	−1.77
meta	0.97	1.99	1.98	1.07	0.94
para	2.74	−3.09	−1.98	−1.54	−0.99
Total width	20.42	24.52	21.75	17.49	16.29

[a] Calculated by the McConnell relation using Q 30 G.

To determine the value of the angle θ of the 3-phenyl substituent with the benzo[*b*]furanyl part of the radical we have used the INDO method to calculate the hyperfine splitting constants for angles of 0, 12.5, 25, 37.5, and 50°. The coupling constants calculated for θ 0 and the intermediate value 37.5° are summarized in Table 2. One can observe that the overall splitting is better for θ 37.5 than for θ 0°; in the two cases we find $a_{ortho} > a_{para}$.

If we take the *ortho* : *para* ratio as a measure of the accuracy of the MO calculations the best agreement between experimental ($a_o : a_p$ 0.91) and theoretical values is obtained for a planar structure ($a_o : a_p$ 1.10). This ratio increases with the angle of twist ($a_o : a_p$ 1.26 for θ 37.5°). Similar results are observed for INDO calculations on the benzyl radical.[4,5] Thus in the case of the triphenylmethyl radical [6] the experimental *ortho* : *para* ratio is also 0.91 but ^{13}C n.m.r. coupling constants indicate a deviation from planarity (*ca.* 25°). So we conclude that if radical (II) is not planar, the angle of twist cannot be very important and is certainly less than 25°.

The McLachlan method has been modified according to the procedure described by Honeybourne [3b] for non-alternant radicals containing a heteroatom. The Coulomb integral for the oxygen atoms was taken as $\alpha_O = \alpha_C + h\beta_{C-C}$ where $h_1 > h_{10}$ because the ring oxygen atom has two π-electrons involved in conjugation. We varied h_1 between 2 and 2.8 and h_{10} in the range 1.4—2.6 using all the combinations for which $h_1 > h_{10}$. These variations have a small influence upon the distribution of spin densities. The following values were used in the calculations: $h_1 = 2.2$ and $h_{10} = 1.7$. The resonance integrals were expressed as $\beta_{C-O} = k\beta_{C-C}$ where (*cf.* ref. 7) $k_{2\text{-}10} = 1.32$, $k_{1\text{-}2} = k_{1\text{-}8} = 0.6$, and $k_{2\text{-}3} = 1$. The variation of $k_{1\text{-}2}$ and $k_{1\text{-}8}$ in the 0.5—0.8 range has a very small influence upon the results. According to Dewar,[8] we have used the following equation for the C_3–C_{11} bond: $\beta = \cos\theta$ with $k_{3\text{-}11} = 0.75$. This value takes into account the 37.5° angle between the two planes and the bond length. For θ = 0, we have chosen $k_{3\text{-}11}$

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[2] (*a*) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026; (*b*) J. A. Pople and D. L. Beveridge, *J. Amer. Chem. Soc.*, 1968, **90**, 4201.

[3] (*a*) A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233; (*b*) C. L. Honeybourne, *ibid.*, 1971, **21**, 1057; *Tetrahedron Letters*, 1971, **52**, 4927.

[4] H. Fischer, *Z. Naturforsch.*, 1965, **20**, 488.

[5] J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 1968, **49**, 4725.

[6] K. Schreiner, A. Berndt, and F. Baer, *Mol. Phys.*, 1973, **26**, 929.

[7] A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1962, ch. 5.

[8] M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3345.

0.84. The usual value of 1.2 [3a] was used for the parameter λ. The spin densities calculated according to this method are summarized in Table 2. The theoretical coupling constants have been calculated using the McConnell relation with Q 30 G.

If one compares the theoretical values obtained by the various methods with the experimental data, it becomes clear that none of the calculations gives truly good results (Table 2). The results obtained by the INDO and McLachlan methods give an almost correct order of coupling constants, with one exception. According to the calculations, the spin density should be higher on C-4 than on C-6. The experimental data indicate the opposite. This observation is not surprising, however, because similar cases have already been documented.[9]

Conclusions.—As far as we know, radical (II) is the first stable benzofuranyl radical described. It is a totally asymmetric radical. Because of this we were able to evaluate the limitations of spin density calculations. It can be concluded that none of the methods used gives a rigorous assignment of the coupling constants to the positions of the radical. It is therefore necessary to have experimental data for this purpose. We have studied various methylated derivatives of DTDB. The methyl groups were used to label the different positions in the radical.

TABLE 3

Acids and phenols used to prepare methylated monomers used in formation of analogues of (I)

Acid	Phenol	Position of methyl group	M.p. (°C)
Mandelic	*p*-Cresol	5	106—107
Mandelic	*m*-Cresol	6	122—123
Mandelic	*o*-Cresol	7	65—66
m-Methylmandelic	Phenol	*m*	90—92
p-Methylmandelic	Phenol	*p*	96—97
Mandelic	2,5-Dimethylphenol	4, 7	100—102
Mandelic	3,4-Dimethylphenol	5, 6	93—94
Mandelic	2,3-Dimethylphenol	6, 7	96—119
p-Methylmandelic	*m*-Cresol	6, *p*	118—119
[$^2H_5$]Mandelic	Phenol		114—116

TABLE 4

		Elemental analysis						
		Calc. (%)			Found (%)			
Product	δ_{Me} [a]	C	H	O	C	H	O	M.p. (°C)
7,7'-Dimethyl-DTDB	2.3	80.7	5.0	14.35	80.7	4.9	14.2	220—230
3,3'-Di-*p*-tolyl-DTDB	2.32	80.7	5.0	14.35	80.7	5.0	14.15	178—184
3,3'-Di-*m*-tolyl-DTDB	2.26	80.7	5.0	14.35	80.9	5.2	14.25	177—180
5,5',6,6'-Tetramethyl-DTDB	2.18—2.30	81.0	5.5	13.5	80.65	5.95	13.65	193—202
6,6' 7,7'-Tetramethyl-DTDB	2.18—2.28	81.0	5.5	13.45	80.75	5.45	13.45	195—205

[a] Chemical shifts of methyl protons (tetramethylsilane as standard).

EXPERIMENTAL

Synthesis of DTDB (I) *and its Methyl Derivatives*.—DTDB was obtained from its monomer, 2-oxo-2,3-dihydro-3-phenylbenzo[*b*]furan. The latter was synthesized by condensation of mandelic acid and phenol according to Arventiev.[10] Cresols were used to form derivatives methylated on the benzo[*b*]furan system. For the synthesis of derivatives methylated in the 3-phenyl substituent, *m*- or *p*-methylmandelic acid was used. These were formed by hydrolysis of ω,ω'-dibromo-*m*- or -*p*-methylacetophenone. Table 3 lists the products from which the various methylated monomers were synthesized. DTDB and its derivatives were obtained by condensation of two monomeric molecules according to the method described by Löwenbein.[11]

Monomer synthesis. A mixture of mandelic acid (1 mol) and phenol (1 mol) was heated at 180—190 °C for 30 min, water was added, and the mixture was cooled until the oil solidified. The solid was then washed with water. Unchanged phenol was removed by steam-distillation, the crude product was washed with 2N-sodium carbonate solution, dissolved in ethanol, and crystallized. The methylated derivatives were synthesized by the same process.

Synthesis of DTDB (I). Monomer (3 g) was dissolved in dry ether (75 ml). Sodium was added in small excess and the solution was heated under reflux for 5—8 h. The solution which in some cases contained some unchanged sodium was separated and iodine (0.5 equiv.) dissolved in dry ether was added. The precipitated sodium iodide was filtered off, the solution washed with a 1N solution of sodium thiosulphate, and evaporated until the volume was reduced to 15 ml. The solution was cooled and the precipitated DTDB filtered off and washed with ethanol. It was recrystallized from ether or furan.

Synthesis of perdeuteriated m- *or* p-*methylmandelic acid*. These syntheses have been carried out by hydrolysis of the corresponding perdeuteriated ω,ω'-dibromo-*m*- or -*p*-methylacetophenones.

Hydrolysis was performed with 10% KOH solution by shaking until all the starting compound was dissolved in the water phase. It was then neutralized by hydrochloric acid. The methylmandelic acid which precipitated was filtered off, extracted with ether, and recrystallized from benzene, m.p. *para*-acid, 144—146°; *meta*-acid, 94—96°. Perdeuteriophenylacetophenone was synthesized by acylation of [$^2H_6$]benzene.[12] Bromination of acetophenone was performed by bromine in acetic acid at 25 °C.[13]

6-*Methyl-DTDB*. The synthesis of this compound has been carried out using the above method. The monomer of 4-methyl-DTDB was also formed in small amount. The monomer of 6-methyl-DTDB was purified by recrystallization from ethanol, m.p. 122—123°.

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[9] F. Bruin, F. W. Keineken, and M. Bruin, *J. Org. Chem.*, 1963, **28**, 562.

[10] B. Arventiev, *Ann. St. Univ. Jassi*, 1938, (I)**24**, 72.

[11] A. Löwenbein, *Ber.*, 1925, **58**, 601.

[12] *Org. Synth.*, 1961, Coll. Vol. I, 109.

[13] Beilstein, vol. VII, p. 309.

Analytical and spectroscopic data on new compounds are summarized in Table 4. The large melting range of some DTDB derivatives is due to the formation of radicals during heating.

Calculations.—INDO Calculations were performed using a program of Pople and Beveridge.[14] Calculation of spin densities and computer simulation of the e.s.r. spectra were performed on a CII-10070 computer of the Centre Interuniversitaire de Traitement de l'Information, Lille.

[6/1895 *Received*, 11*th October*, 1976]

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[14] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.