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SPIRANES—IV[1]

LONG RANGE SHIELDING EFFECTS BY BENZENE, THIOPHENE AND FURAN RINGS IN THE PROTON MAGNETIC RESONANCE SPECTRA OF DIARYLSPIROKETONES[2]

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Abstract—The proton NMR spectra of several diphenyl, dithienyl and difurylspiroketones have been analysed and compared with the spectra of the analogous spiroketones without aryl groups. The comparison reveals that the two benzene, thiophene and furan rings in the diarylspiroketones exert a strong shielding effect upon protons at distances of 3–4 Å from the aryl rings. The effect is most marked in the diphenylspiroketones B, E and G (Table 2), in which the methyl protons exhibit shifts of 0·01–0·08 ppm downfield from tetramethylsilane. The extra upfield shift ($\Delta\delta$) which the protons or methyl protons at position 3 undergo amounts to 0·95–1·45 ppm for the diphenylspiroketones from Table 2 and 0·58–1·07 ppm for the dithienyl and difurylspiroketones from Table 3. These appear to be the first examples of long range *shielding* effects exhibited by heterocyclic aromatic rings. The ratio of ring currents in benzene, thiophene and furan as determined by their shielding effects (100:77:60, Table 5) agrees well with the same ratio as estimated from the *de*shielding values of these aromatics and their methyl derivatives (Table 7). The shielding values, predicted from the graphs of Johnson and Bovey are in good agreement with the observations.

The axial protons α to the carbonyl group in the diarylcyclohexanone rings absorb 0·85–1·1 ppm further *downfield* from their equatorial counterparts.

INTRODUCTION

THE ring current induced into the π electrons of a benzene ring by an external magnetic field exerts a *de*shielding effect on protons situated in or near the plane of the ring while protons situated above or below the ring are shielded. In this publication we will restrict ourselves to the diamagnetic *shielding* effect which shifts the signals due to protons above or below the ring to *higher* field strengths. The matter has been well reviewed.[3–6] The following review includes more recent examples of the long range shielding effect caused by the benzene ring. The numbers in parentheses represent the shift differences ($\Delta\delta$, ppm) between the signals of the shielded protons in the aromatic compound and of similar protons in an analogous compound without

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[1a] Part I: H. A. P. de Jongh and Hans Wynberg, *Rec. Trav. Chim.* **82**, 202 (1963);

[b] Part II: H. A. P. de Jongh and Hans Wynberg, *Ibid.* **82**, 602 (1963);

[c] Part III: H. A. P. de Jongh and Hans Wynberg, *Tetrahedron* **20**, 2553 (1964).

[2] Partly taken from H. A. P. de Jongh, *Synthesis of mono- and polyspiranes consisting of cyclohexane rings* Chap. II. Groningen (1964). Communicated on the NMR symposium, organized by the Organic Section of the Royal Dutch Chemical Society at Wageningen in April 1964.

[3] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* pp. 115 and 125–129. Pergamon Press, London (1959).

[4] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High resolution Nuclear Magnetic Resonance* pp. 180–183. McGraw-Hill, New York, N.Y. (1959).

[5] H. Conroy, *Advances in Organic Chemistry* (Edited by R. A. Raphael, E. C. Taylor and H. Wynberg) Vol. II; pp. 281–284. Interscience, New York, N.Y. (1960).

[6] W. D. Phillips, *Determination of Organic Structures by Physical Methods* (Edited by F. C. Nachod and W. D. Phillips) Vol. 2; pp. 407–411. Academic Press, New York and London (1962).

benzene rings or between two isomers with different orientations of the benzene rings, e.g. *cis* and *trans* isomers. The recent examples include the following types of compounds containing benzene rings: alkaloids[5] (0·7), diaryl ethers,[7] diaryl thioethers[8] (0·5–0·8), *para*cyclophanes[9,10] (0·6–0·8), α,α'-dimethylstilbenes[11] (0·2–0·3), biaryls[3,12] (0·2), doubly bridged biphenyls[13] (0·2–0·3), phenylcyclohexanes[14] (0·2–0·3), 15,16-dimethyldihydroperylene[15] (5·2), 3,3-dialkylphtalides[16] (0·5–0·8), arylsulphonylnorbornenes[17] (1·1), benzonorbornadienes[18] (0·2–0·3), diarylcyclopentanes[19] (0·3–0·6), 3,4-diaryladipic esters[19] (0·1–0·3), benzospiranes[19a] (0·6) and phenyl-β-lactams[20] (0·7). The case of 15,16-dimethylperylene[15] deserves special comment: the methyl groups are internal to the π-electron cloud. However, the aromatic system bears more resemblance to a 14-annulene[21] than to a benzene ring.

Waugh and Fessenden have calculated the shielding due to the π-electron circulations in the benzene nucleus.[9] They have tabulated this shielding for the region around the benzene ring in ppm, using the cylindrical coordinates ρ and z. The same calculations have been refined and represented graphically by Johnson and Bovey.[22] These graphs or tables can be used to predict the conformation of an aromatic compound. Measurements on Dreiding models give the ρ and z values of the shielded proton for various conformations. The tables or graphs give the theoretical shielding value (ppm) belonging to these coordinates. Comparison of these values with the shielding found in the NMR spectrum gives the most probable conformation.[3,7,9,11,17,20,22,23]

No examples of long range *shielding* effects by heterocyclic aromatic rings are recorded.

RESULTS AND DISCUSSION

The preparation of most of the spiro ketones with or without a phenyl group (Tables 2 and 4) *via* a double Michael reaction between dibenzalacetone or divinyl ketone and cyclohexane-1,3-diones has been described in papers I and II of this series.[1a,c] The synthesis of the new dithienyl- and difurylspiroketones from Table 3 via a double Michael reaction between 1,5-bis(2-thienyl)pentadien-3-one or 1,5-bis(2-furyl)pentadien-3-one and cyclohexane-1,3-diones can be summarized in

[7] H. Shimizu, S. Fujiwara and Y. Morino, *J. Chem. Phys.* **34**, 1467 (1961).

[8] H. Agahigian and G. D. Vickers, *J. Org. Chem.* **27**, 3324 (1962).

[9] J. S. Waugh and R. W. Fessenden, *J. Amer. Chem. Soc.* **79**, 846 (1957).

[10] D. J. Cram and M. Goldstein, *J. Amer. Chem. Soc.* **85**, 1063 (1963).

[11] N. Inamoto, S. Masuda, Y. Nagai and O. Simamura, *J. Chem. Soc.* 1433 (1963).

[12] A. Mannschreck, H. A. Staab and D. Wurmb-Gerlich, *Tetrahedron Letters* 2003 (1963).

[13] K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon and G. H. Wahl, Jr., *J. Amer. Chem. Soc.* **86**, 1710 (1964).

[14] E. W. Garbisch, Jr., and D. B. Patterson, *J. Amer. Chem. Soc.* **85**, 3228 (1963).

[15] V. Boekelheide and J. B. Phillips, *J. Amer. Chem. Soc.* **85**, 1545 (1963).

[16] G. C. Brumlik, R. L. Baumgarten and A. I. Kosak, *Nature Lond.* 388 (1964).

[17] H. Hogeveen, G. Maccagnani, F. Montanari and F. Taddei, *J. Chem. Soc.* 682 (1964).

[18] K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji and H. Tanida, *Canad. J. Chem.* **42**, 926 (1964).

[19] D. Y. Curtin and S. Dayagi, *Canad. J. Chem.* **42**, 867 (1964).

[19a] H. H. Inhoffen, D. Kampe, C. Cordes, K. D. Müller and W. Milkowski, *Liebigs Ann.* **674**, 36 (1964).

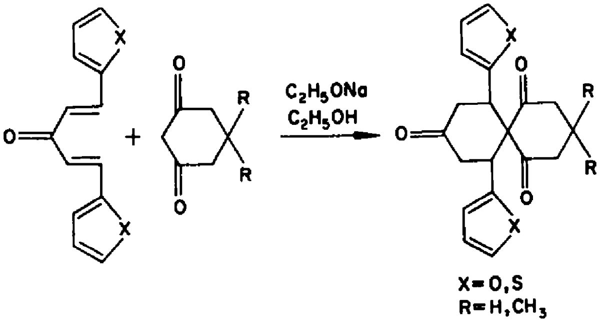
[20] H. B. Kagan, J. J. Basselier and J. L. Luche, *Tetrahedron Letters* 941 (1964).

[21] L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky and A. A. Bothner-By, *J. Amer. Chem. Soc.* **84**, 4307 (1962).

[22] C. E. Johnson, Jr. and F. A. Bovey, *J. Chem. Phys.* **29**, 1012 (1958).

[23] E. W. Garbisch, Jr., *J. Amer. Chem. Soc.* **85**, 927 (1963).

the following reaction equation:



Moreover the model compounds E, G and I have not been described earlier. The structures of the new compounds are supported by the elementary analyses, mol. wts, IR, UV and NMR spectra (Experimental).

All of the NMR spectral data together with the structural formulae are recorded in Tables 1–4, while the most representative spectra are reproduced in Fig. 1. The numbering of the carbon atoms in the 2,2-dialkylcyclohexane-1,3-diones (H, I, R and S) is not in agreement with the official rules but allows a better mutual comparison. Changing the concentration of compound B in carbon tetrachloride from 5% over 17% to 50% did not affect the chemical shift within the experimental error (1%). For this reason we did not extrapolate the chemical shifts to infinite dilution.

We now turn to a systematic discussion of the NMR spectra, going from high to low δ values.

Aryl protons

The phenyl protons of the compounds in Table 2 all give a complicated multiplet with the strongest peak in the narrow region δ 7·08–7·20. The thienyl protons in the compounds J–L show a quartet at δ 7·07–7·13; a doublet at δ 6·90 and a multiplet at δ 6·73–6·77, which are respectively ascribed to the protons at positions 5′, 4′ and 3′ (Fig. 1). The pattern is very similar to that of 2-methylthiophene.[24] The furyl groups of the difurylspirotriketones M and N exhibit a band at δ 7·30, a multiplet at δ 6·30 and a doublet at δ 6·02, which can be respectively ascribed to the protons at positions 5′, 4′ and 3′. The pattern is similar to that of 2-methylfuran.[25]

Protons at positions 7, 8, 10 *and* 11

The hydrogens at positions 7, 8, 10 and 11 will henceforth be indicated by H_7, H_{8a} (axial), H_{8e} (equatorial), H_{10a} (axial), H_{10e} (equatorial) and H_{11}. The protons at positions 7, 8, 10 and 11 of the diarylspiroketones in Tables 2 and 3 give two identical ABX systems. In case of the compounds D, E, J, K, L, M and N, the ABX spectrum simplifies to an AMX system,[26] because $(\nu_A - \nu_B)/J_{AB} > 2$. Simple zero-order AMX treatment in these cases gives approximately the same coupling constants as a more

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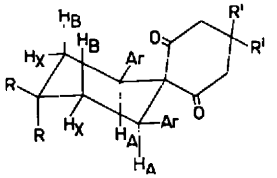
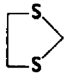
[24] N. S. Bhacca, L. F. Johnson and J. N. Shoolery, *NMR Spectra Catalog* Varian Associates, Palo Alto, California (1962).

[25] S. Gronowitz, G. Sörlin, B. Gestblom and R. A. Hoffman, *Ark. f. Kemi* **19**, 483 (1963); G. S. Reddy and J. H. Goldstein, *J. Phys. Chem.* **65**, 1539 (1961).

[26] J. D. Roberts, *Spin–Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra* pp. 63–65. W. A. Benjamin, New York (1961).

elaborate ABX calculation. Table 1 gives the coupling constants for both treatments in case of the compounds D, K and N. The ABX treatment gives opposite signs of J_{AX} and J_{BX}, in accord with several examples in the literature in which vicinal and geminal coupling constants are found to be of opposite sign.[27] The geminal coupling constant for sp^3 hybridized methylene groups has recently been considered of negative sign.[28,28a] This is also reflected in Table 1. The non-equivalence of the line intensities points to a certain amount of ABX character of the AMX systems, as a pure AMX system should consist of twelve lines of equal intensity.[26] Conversion of the 9-keto group of the diphenylspirotriketones A and B into a thioketal group (thioketals D and E) increases the difference in chemical shift between the A and B part of the ABX pattern from 0·22 ppm to 0·42–0·85 ppm. This gives a transition of the ABX system to an AMX system and can be observed by comparing the spectra of A and D (Fig. 1).

TABLE 1. COUPLING CONSTANTS OF THE PROTONS ON POSITIONS 7, 8, 10 AND 11 OF SOME DIARYLSPIROKETONES*

		Treatment	J_{AB} cps	J_{AX} cps	J_{BX} cps	$\nu_A-\nu_B$ cps
Ar: Ph R, R: O=	(B)†	ABX	13·8	3·4	−13·6	13·3
Ar: Ph R, R: 	(D)	ABX	12·2	3·2	−14·0	23·4
		AMX	12·8	2·2	−12·8	26·5
Ar:  R, R: O=	(K)	ABX	14·1	4·9	−15·2	35·6
		AMX	14·1	3·8	−14·1	36·0
Ar:  R: CH$_3$S	(L)	AMX	13·1	3·3	−14·0	75·5
Ar:  R, R: O=	(N)	ABX	13·9	5·0	−15·5	26·2
		AMX	14·0	3·0	−14·0	27·4

* See remarks under Table 2.

† Calculated from the spectrum in benzene solution.

The position of the aryl protons (at carbon atoms 7 and 11) of the compounds B and K has been established by deuterium exchange in deuterated ethanol containing some sodium (Experimental). In both cases, the absorptions ascribed to the four

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[27] B. D. Nageswara Rao, J. D. Baldeschwieler and J. I. Musher, *J. Chem. Phys.* **37**, 2480 (1962).

[28] T. Takahashi, *Tetrahedron Letters* 565 (1964).

[28a] F. Hruska, T. Schaefer and C. A. Reilly, *Canad. J. Chem.* **42**, 697 (1964).

protons at positions 8 and 10 disappears almost completely. In the deuterated compound B, the remaining absorption coincides exactly with the strongest peak in the ABX pattern (δ 3·72; see Fig. 1), while in the deuterated triketone K, the remaining absorbtion coincides with the center of the quadruplet at δ 4·03. The assignment of the aryl protons is further confirmed by inspection of the shifting that takes place when the 9-keto groups of the diarylspirotriketones A, B and K are converted to thioketal groups (compounds D, E and L). The absorption due to the aryl protons is shifted a little to lower field (0·1–0·2 ppm) or remains almost constant, while the four protons at positions 8 and 10 all undergo a shift of 0·3–0·5 ppm to higher field. It is evident that conversion of the 9-keto group to a thioketal group must affect the protons α to the carbonyl group much more than the β protons.

The assignment of the center part (B part) of the ABX systems to the *axial* protons and the quadruplet at highest field to the *equatorial* proton at positions 8 and 10 is based upon a consideration of the coupling constants. Reported values for J_{gem} (geminal coupling constant) range from 12–15 c/s,[29] while methylene groups α to carbonyl groups often show a marked increase in J_{gem}[28] (up to 20 c/s), Huitric *et al.* have recently reviewed axial–axial and axial–equatorial coupling constants (J_{aa} and J_{ae}) in six membered ring compounds.[30] Their values for various phenylcyclohexanes range from 9·5–12·4 c/s for J_{aa} and 1·9–4·2 c/s for J_{ae}. The triplet assigned to H_{8a} and H_{10a} in the spectra of compounds E, and J–N arises from two strong, almost *equal* couplings with H_7 and H_{11} and with H_{8e} and H_{10e}.

Table 1 shows values of J 12·2–14·1 c/s for the one coupling constant and values of 12·8–15·5 c/s for the other. These couplings can only be J_{aa} and J_{gem} and consequently H_{8a} and H_{10a} absorb at the lowest field. The remaining quartet is due to H_{8e} and H_{10e}, which are weakly coupled with the aryl protons (J_{ae} 2·2–5·0 c/s, Table 1). The absorption of the axial protons α the 9-carbonyl group at a downfield position from the equatorial protons is in accord with an apparently general rule for the protons α to the carbonyl group in cyclohexanones.[31] This rule is now extended to thioketals. The unusual large difference in chemical shifts between the axial and equatorial protons at positions 8 and 10 (0·85–1·1 ppm) as compared with the values found (0·2–0·5 ppm)[31] can be understood by inspection of the molecular models.

The NMR spectral data clearly point to a rigid diaryl cyclohexane ring in which the two aryl groups adopt an equatorial position. The Dreiding model (Fig. 2) and the Stuart–Briegleb model of the diphenylspirotriketones A–C show a striking similarity in spatial arrangement between all of the *axial* protons at positions 7, 8, 10 and 11. This is partly due to the angle (<90°) which the phenyl groups make with the "plane" of the cyclohexane ring carrying the phenyl groups. This angle results from a steric interaction with the hydrogen atoms at positions 2 and 4 of the mobile cyclohexanedione ring. Moreover, all of the axial protons at positions 7, 8, 10 and 11 are almost equally surrounded by carbonyl groups. An estimation of the deshielding influence of the benzene rings on the axial protons at positions 7, 8, 10 and 11, using

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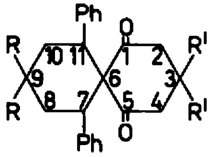
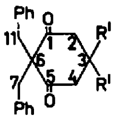
[29] Ref. 3, p. 85.

[30] A. C. Huitric, J. B. Carr, W. F. Trager and B. J. Nist, *Tetrahedron* **19**, 2145 (1963).

[31] K. L. Williamson and W. S. Johnson, *J. Amer. Chem. Soc.* **83**, 4623 (1961); K. M. Wellman and F. G. Bordwell, *Tetrahedron Letters* 1703 (1963); A. Nickon, M. A. Castle, R. Harada, C. E. Berkoff and R. O. Williams, *J. Amer. Chem. Soc.* **85**, 2185 (1963); B. Waegell, *Bull. Soc. Chim. Fr.* 855 (1964); E. W. Garbisch, Jr., *J. Amer. Chem. Soc.* **86**, 1780 (1964).

Table 2. NMR spectral data* of diphenylspiroketones and 2,2-dibenzylcyclohexan-1,3-diones



				δ values for protons at positions†							
				AB		X syst.					Δδ‡
				7·11	8,10(a)	8,10(e)	2,4		3(qn)	CH_3(s)	3/CH_3
O=	„	H H	(A)	3·70	3·48	2·40	1·88 1·68	t t	0·58		1·37
O=	„	CH_3 CH_3	(B)	3·72	3·50	2·42	1·95 1·55	s s		0·08	0·95
O=	„		(C)	3·72	3·50	2·42	1·97 1·57	s s	1·02 (β)	0·20 (α)	1·25 (α)
	„	H H	(D)	3·65	3·22	2·10	1·68	t	0·52		1·43
CH_3S CH_3S	„	CH_3 CH_3	(E)	3·93	3·08	masked	1·78 1·58	s s		0·04	0·99
H H	„	H H	(F)	3·30	unresolved		1·65	t	0·50		1·45
H H	„	CH_3 CH_3	(G)	3·28	unresolved		1·72 1·53	s s		0·01	1·02
											
	„	H H	(H)	3·22			1·80	t	0·80		1·10
	„	CH_3 CH_3	(I)	3·13			1·87	s		0·23	0·75

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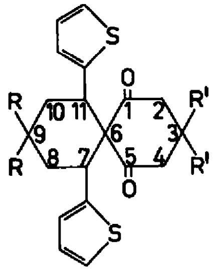
* Determined with a Varian A–60 spectrometer from 5 to 20% solutions in carbon tetrachloride. The δ values are expressed in ppm from tetramethyl-silane as an internal standard.

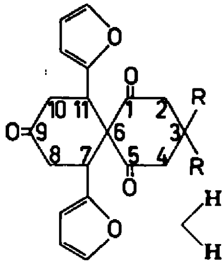
† *Abbreviations*: a = axial, e = equatorial, s = singlet, t = triplet, qn = quintuplet.

‡ Difference in δ values of the protons or methyl protons at position 3 between analogous compounds without and with aryl groups (e.g. O and A, P and B etc.).

the graphs given by Johnson and Bovey[22] (see also Introduction) gives extra shifts between —0·5 and —0·7 ppm, while the deshielding of the two equatorial protons at positions 8 and 10 is calculated to be —0·2 ppm. Indeed, we find that H_{8e} and H_{10e} absorb about 0·2 ppm downfield from the α protons in cyclohexanone (δ 2·25 ppm).

TABLE 3. NMR SPECTRAL DATA* OF DITHIENYL- AND DIFURYLSPIROKETONES



				δ-values for protons at positions							Δδ
				AM		X syst.					
				7,11	8,10(a)	8,10(e)	2,4		3(qn)	CH_3(s)	3/CH_3
O=	”	H H	(J)	4·03	3·38	2·53	2·03 1·98	t t	0·88		1·07
O=	”	CH_3 CH_3	(K)	4·03	3·40	2·53	2·05 1·87	s s		0·28	0·75
CH_3S CH_3S	”	CH_3 CH_3	(L)	4·16	2·95	2·00	1·88	s		0·25	0·78
		H H	(M)	3·93	3·38	2·53	2·28 2·13	t t	1·17		0·80
	”	CH_3 CH_3	(N)	3·92	3·45	2·52	2·08 2·05	s s		0·45	0·58

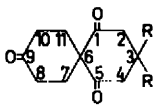
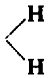
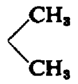
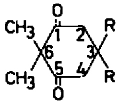
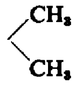
* See remarks under Table 2. The spectra of compounds M and N were measured in deuterochloroform due to extreme insolubility in CCl_4.

Taking the normal difference in chemical shifts between axial and equatorial α protons in cyclohexanones to be 0·2–0·5 ppm,[31] we would expect a difference of 0·5–1·0 ppm for the axial and equatorial protons at positions 8 and 10 in the diphenylspirotriketones. This is in good agreement with the observed differences for compounds A–C (1·08 ppm). The axial and equatorial protons at positions 8 and 10 of the dithienyl and difuryl spiroketones from Table 3 show the same shift difference, i.e. 0·85–0·95 ppm, while the two equatorial protons have undergone a shift to lower field of only 0·3 ppm compared with cyclohexanone (δ 2·25).

Protons at positions 2 *and* 4

Dreiding models of the diphenylspirotriketones (Figs. 2, 3 and 4) clearly show that the protons at positions 2 and 4 are situated closely above the aromatic ring and we expect a strong shielding effect. Comparison of the data for the positions 2 and 4 between the diaryl compounds of Tables 2 and 3 and the analogous dialkyl compounds of Table 4 shows an extra shift to higher field of 0·65–1·07 ppm for the diphenyl compounds and of 0·52–0·73 ppm for the dithienyl- and difurylspiroketones. In case of the diphenylspiroketones an extra shift of about 0·7–0·9 ppm can be calculated from the graphs given by Johnson and Bovey.[22] This calculation is based upon a conformation of the cyclohexane-1,3-dione ring which is intermediate between the two chair forms (Fig. 3).

TABLE 4. NMR SPECTRAL DATA* OF SPIROTRIKETONES AND 2,2-DIMETHYLCYCLOHEXAN-1,3-DIONES

		δ values for protons at positions‡:				
		7,8,10,11	2,4†	3†	CH_3(6)	CH_3(3)
„ 	(O)	2·27 m	2·70 t (2·77)	1·95 t (1·97)		
„ 	(P)	2·27 m	2·60 s (2·70)			1·03 (1·03)
	(Q)	2·27 m	2·63 m	1·45 γ		
						
„ 	(R)		2·63 t	1·90 m	1·22	
„ 	(S)		2·55		1·22	0·98

* See remarks under Table 2.

† The δ values in parentheses were determined in $CDCl_3$ as solvent.

‡ m means multiplet. The protons on positions 7, 8, 10 and 11 give an A_2B_2 multiplet.

It is noteworthy that the protons at positions 2 and 4 are not equivalent in many of the diarylspiroketones. Thus, when two methyl groups are present at position 3,

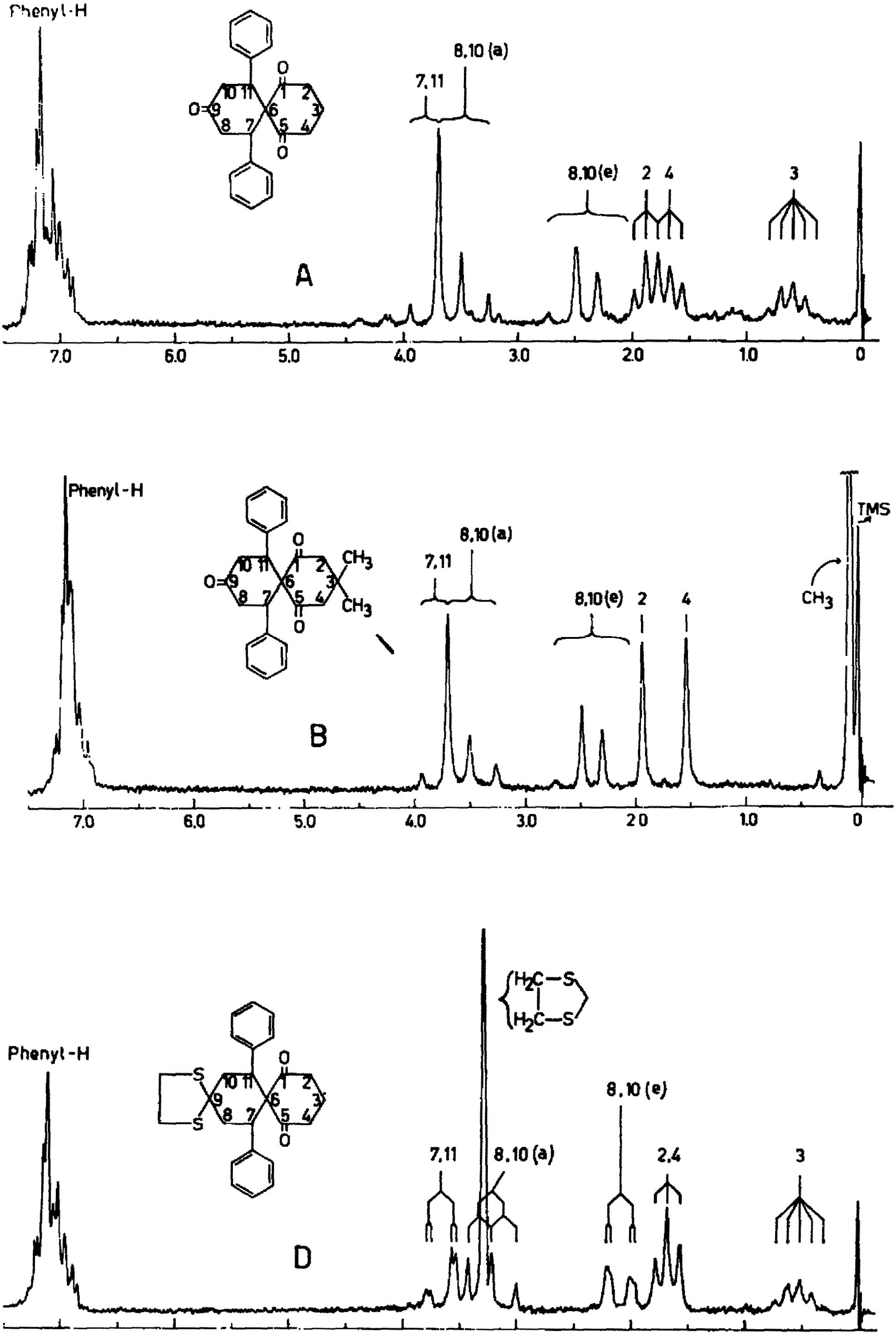


FIG. 1 (Continued on next page).

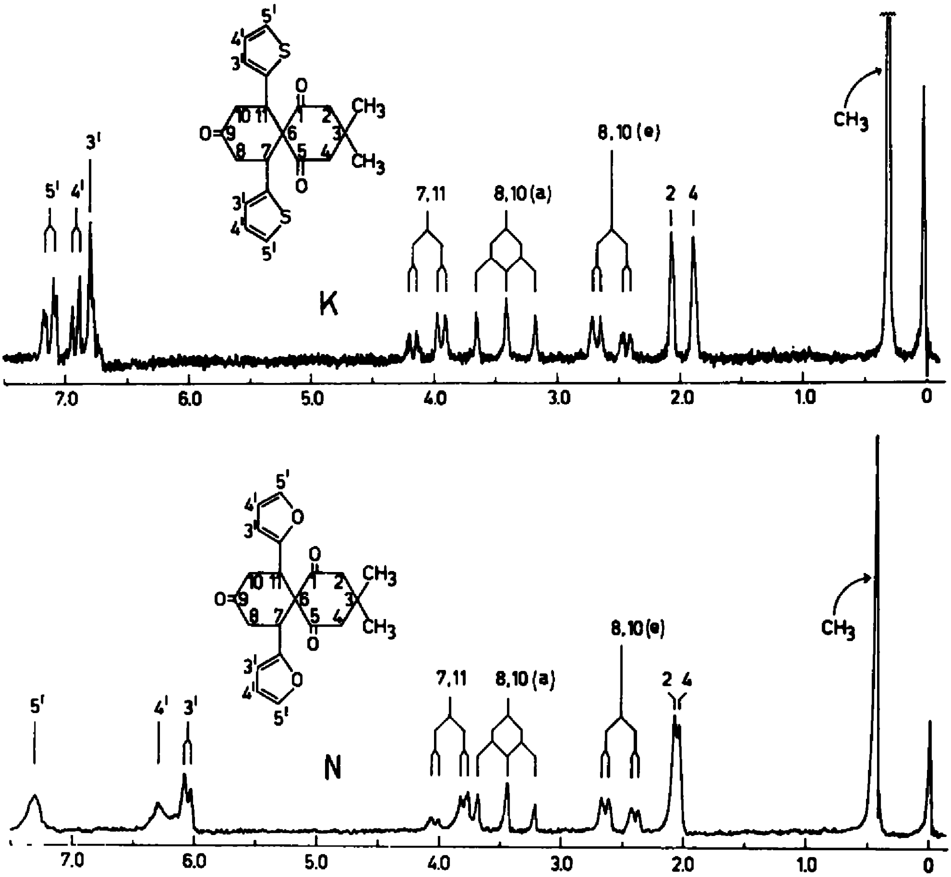


Fig. 1. PMR spectra of the diarylspiroketones A, B, D, K and N. For details, see remarks under Table 2.

the protons at positions 2 and 4 give one singlet only in case of compound L, while in all other cases we see *two* singlets separated by 0·18–0·40 ppm. When carbon atom 3 carries no substituents we observe one triplet in case of compounds D and F, while compounds A, J and M give *two* triplets separated by 0·05 to 0·20 ppm. All triplets show the same coupling constant, i.e. J = 6 c/s. An explanation of the non-equivalence of the protons at positions 2 and 4 by a rigidity of the cyclohexanedione ring, leading to a non-equivalence of the axial and equatorial protons, must be excluded absolutely. A rigid cyclohexanedione ring would give an AB or AX pattern (J_{gem} = 12–15 c/s)[29] in case of the 3,3-dimethyldiarylspiroketones, while an ABXY system would be predicted in case of the diarylspiroketones with no 3-alkyl substituents. The spectra contradict these expectations. A calculation of the shielding effects by the benzene nuclei in case of a *rigid* cyclohexanedione ring gives differences of 2–3 ppm between the axial and equatorial protons at positions 2 and 4! The largest difference found is only 0·4 ppm. Furthermore the absorption pattern due to the protons at positions 2, 3 and 4 is identical in the thioketal D and the 2,2-dibenzylcyclohexane-1,3-dione H, which certainly has a mobile ring.

The spectrum of compound B, taken at various temperatures between −80° (in carbon disulfide) and 140° (in pentachloroethane) did not show significant changes, apart from the usual line broadening at low temperatures. The available data do not allow a choice between a rapid chair–chair equilibrium as shown in Fig. 3 or an intermediate "flexible form"[32] (e.g. a twist boat or a flattened chair).

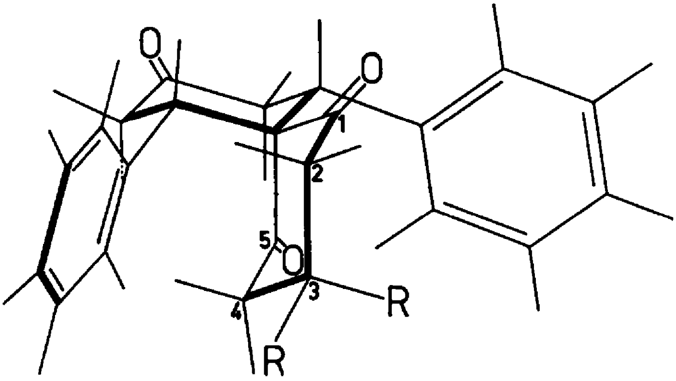


FIG. 2. Dreiding model of the diphenylspirotriketones A–C.

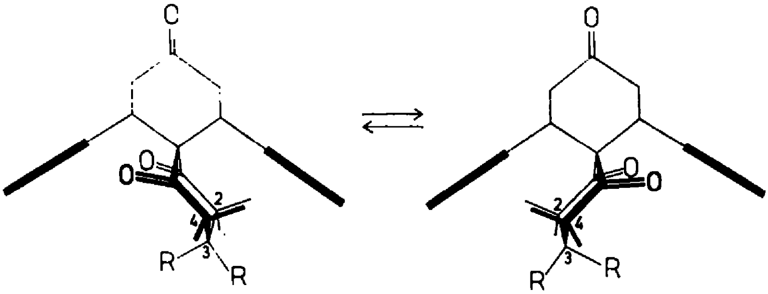


FIG. 3. Chair–chair equilibrium of the cyclohexanedione ring in the diphenylspirotriketones A–C. The model clearly shows the positions of the shielded protons or methyl protons at carbon atoms 2, 3 and 4 *above* the benzene rings.

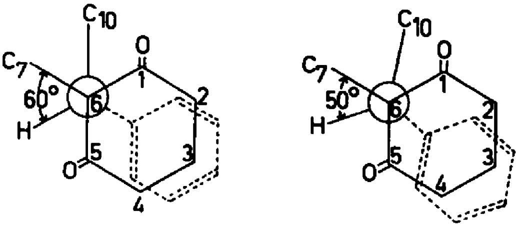


FIG. 4. Newman projection of the diphenylspiroketones from Table 2 along the C_6—C_{11} bond, showing the possibility of a (non)-equivalence of the 2- and 4-methylene groups. The left picture refers to the compounds with a 9-thioketal group or a 9-methylene group. The right picture refers to the compounds with a 9-carbonyl group. The transition from left to right corresponds with a *flattening* of the diphenylcyclohexane ring (see text).

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[32] E. L. Eliel, *Stereochemistry of Carbon Compounds* pp. 201–207. McGraw-Hill, New York (1962).

The non-equivalence of the protons at positions 2 and 4 is clearly due to a non-equivalence of both methylene groups, which originates from a slightly different position of the 2- and 4-methylene groups relative to the aryl rings.[33] This is shown in Fig. 4.[33] The non-equivalence of the 2- and 4-methylene groups is appreciably influenced by substitution at the 9-position. Thus when the 9-keto group in the diphenylspirotriketone A is converted into a thioketal group (compound D) or into a methylene group (compound F), the difference between the 2- and 4-methylene groups disappears (compare the spectra of A and D, Fig. 1). A similar decrease of the difference between the 2- and 4-methylene groups (from 0·4 to 0·2 ppm) is observed when the 9-keto group of the diphenylspirotriketone B is converted into a thioketal group (compound E) or into a methylene group (compound G) or when the 9-keto group of the dithienylspirotriketone K is converted into a thioketal group (compound L). Altona has pointed out[33] that this decrease of the difference between the 2- and 4-methylene groups can be explained by a decrease in flattening of the diarylcyclohexane ring when the 9-keto group is converted into a thioketal or methylene group. This is due to a change in the hybridization around the carbon atom No. 9 from sp^2 to sp^3. A change in the shape of the rigid diarylcyclohexane ring can cause an appreciable lifting of the phenyl rings. This is shown in Fig. 4 for an angle twist of 10°.

Protons or methyl protons at position 3

The protons or methyl protons at position 3 experience a strong shielding effect from both aryl rings. The last column of Tables 2 and 3 gives the $\Delta\delta$ values, i.e. the extra shifts which the protons or methyl protons at position 3 undergo by the shielding effect of the aryl rings. These values have been obtained by substracting the δ (3-H or CH_3) values of the diaryl spiroketones from the δ (3-H or CH_3) values of the analogous spiroketones without aryl groups. The same method gave the $\Delta\delta$ values for 3-protons or 3-methyl protons of the dibenzylcyclohexanediones H and I.

It should be emphasized that the $\Delta\delta$ values thus obtained represent *total* shielding values composed of shielding by the ring current in the aryl rings and of shielding by the several carbon–carbon double bonds[34] when no ring current would occur. Waugh and Fessenden compare the shifts of the vinyl protons of cyclohexa-1,3-diene which exhibits no ring current with those of benzene. This means that in our case the benzene rings would have to be replaced by cyclohexa-1,3-diene rings in order to account for the ring current only. However, our $\Delta\delta$ values are larger or equal to those calculated from the Johnson and Bovey graphs[22] (see below), which are based upon ring currents only. This suggests strongly that our $\Delta\delta$ values are good measures for the ring current effect of the benzene rings.

With the diphenylspiroketones without substituents at position 3 we observe an extra shift $\Delta\delta$ of 1·37–1·45 ppm to higher field. A calculation of the shielding effect assuming a *flat* cyclohexane-1,3-dione ring (Fig. 5) gives a shielding value of approximately 0·85 ppm for the closer benzene ring and 0·3 ppm for the other benzene ring.

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[33] This explanation was suggested by Dr. C. Altona of the University of Leiden on the occasion of the NMR symposium organized by the Organic Section of the Royal Dutch Chemical Society at Wageningen on April 1964. Dr. Altona also suggested to depict the situation by a Newman projection along the C_6—C_{11} bond, as shown in Fig. 4.

[34] Ref. 3, p. 129.

So we predict a total $\Delta\delta$ of 1·15 ppm, in reasonable agreement with the experimental values.

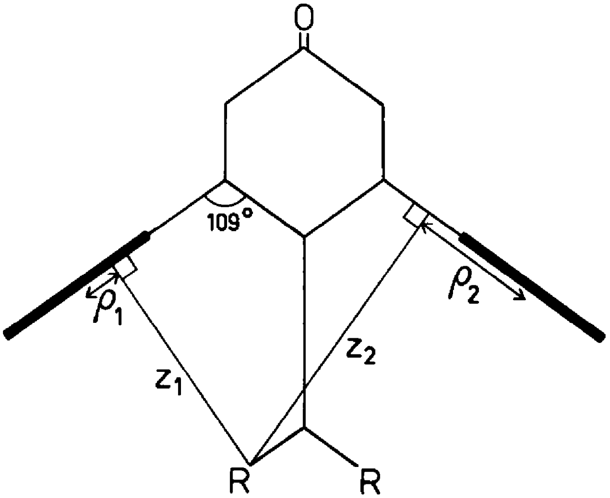

Fig. 5. Geometry of the calculation of the shielding values of the protons or methyl protons at position 3 in the compounds A and B, assuming a *flat* cyclohexanedione ring. The coordinates ρ_1 and z_1 refer to the closer phenyl group, while ρ_2 and z_2 correspond to the remoter phenyl group.

The signal of the methyl protons in the 3,3-dimethyldiphenylspiroketones B, E and G almost coincides with the peak of tetramethylsilane. We observe an extra shift $\Delta\delta$ of 0·95–1·02 ppm to higher field. A calculation of the shielding effect, assuming a *flat* cyclohexane-1,3-dione ring (Fig. 5) gives a shielding value of approximately 0·9 ppm for the closer benzene ring and 0·2 ppm for the other benzene ring. In this case, we predict a total $\Delta\delta$ of 1·1 ppm, which is in good agreement with the experimental values. The shift of the methyl groups was calculated at the position corresponding to the center of the circle described by the free rotation of the methyl group protons. With the diphenyldispiroketone C we observe two broad peaks at δ 1·02 and 0·20 ppm. From these values it is calculated by comparison with compound Q that the far removed β protons still undergo an extra shift $\Delta\delta$ of 0·43 ppm (Table 2). The surprisingly large shift which the 3 protons or 3-methyl protons of the dibenzylcyclohexanediones H and I undergo ($\Delta\delta$ 1·10 and 0·75 ppm) indicates that the phenyl groups in these molecules are oriented in a similar way to those in the more rigid diphenylspiroketones.

The small shiftings to higher field which the protons or methyl protons at position 3 undergo when the 9-keto group is converted into a thioketal group or a methylene group are in agreement with the decrease in the non-equivalence of the 2- and 4-methylene groups. Thus we see that conversion of the diphenylspirotriketone A into the thioketal D or into the diketone F shifts the 3-protons upfield by 0·06–0·08 ppm. Similarly, conversion of the diphenylspirotriketone B into the thioketal E or diketone G shifts the 3-methyl protons upfield by 0·04–0·07 ppm and conversion of the dithienylspirotriketone K into the thioketal L shifts the 3-methyl protons to higher field by 0·03 ppm. This shifting effect can be explained by a lifting of the benzene rings, which causes the 3-protons or 3-methyl groups to situate closer above the benzene rings and together decreases the non-equivalence of the 2- and 4-methylene groups (Fig. 4).

The 3-protons or 3-methyl protons of the dithienyl- and difurylspiroketones undergo less shifting than the equivalent protons in the analogous diphenylspiroketones (Table 3). This can be ascribed to a smaller ring current *and* to a different spatial orientation of the protons considered, relative to the thienyl and furyl nuclei. Stuart–Briegleb models reveal that there is appreciable hindrance to rotation of the aryl rings in the dithienyl- and difurylspiroketones, even when the cyclohexanedione ring has a twist-boat conformation. It is not unreasonable to assume that the thiophene and furan rings adopt a position similar to the benzene rings most of the time. We then can ascribe the difference between the $\Delta\delta$ values in the analogous phenyl-, thienyl- and furyl compounds almost entirely to the difference in ring currents.

TABLE 5. RELATIVE RING CURRENTS IN BENZENE, THIOPHENE AND FURAN

Compounds	Positions	Rel. ring currents benzene	thiophene	furan
A, J, M	2, 4	100	75	61
B, K, N	2, 4	100	75	(74)
A, J, M	3	100	78	58
B, K, N	CH_3	100	79	61
average		100	77	60

Table 5 expresses the relative ring currents of the thiophene and furan rings as evidenced by their shielding effects, against benzene as standard (= 100). The values have been obtained from the ratio of the $\Delta\delta$ values for the protons at positions 2 and 4 (arithmetic mean of the two signals) and for the protons or methyl protons at position 3 of the diarylspirotriketones indicated. The $\Delta\delta$ values of the *difuryl*spirotriketones have been obtained by comparing the spectra of M, N, O and P as determined in deuterochloroform. The $\Delta\delta$ values of the diphenyl- and dithienylspirotriketones from Table 5 were the same when the spectra were run in carbon tetrachloride or in deuterochloroform. Except for the second value for the furan ring, the ratios show internal consistency.

Elvidge and Jackman[35] have advanced the definition of an aromatic compound as a compound which will sustain a ring current and these authors take the magnitude of the ring current as a measure of the aromaticity. In our case, the aromaticity of benzene, thiophene and furan should then be in the proportion 100:77:60. This is in qualitative agreement with the resonance energies of benzene[36] (36 kcal), thiophene[37] (about 20 kcal) and furan[38] (about 17 kcal).

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[35] J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.* 859 (1961).

[36] G. W. Wheland, *Advanced Organic Chemistry* (Third Edition) p. 126. J. Wiley, New York (1960).

[37] S. Sunner, *Acta Chem. Scand.* **9**, 847 (1955). See also S. Gronowitz in *Advances in Heterocyclic Chemistry* (Edited by A. R. Katritzky), Vol. I; p. 19. Academic Press, New York and London (1963).

[38] H. A. Staab, *Einführung in die Theoretische Organische Chemie* pp. 175 and 178. Verlag Chemie Weinheim (1959).

Goldstein and Reddy have used C^{13}—H coupling constants to estimate diamagnetic anisotropy effects in NMR spectroscopy.[39] They arrive at a ring current ratio between benzene and thiophene of 2:1 and claim that the ring current of furan is less than that of thiophene.

Tables 6 and 7 show the results of a determination of the ring currents of thiophene

TABLE 6. DESHIELDING VALUES OF THE AROMATIC PROTONS OR METHYL PROTONS IN BENZENE, THIOPHENE AND FURAN AND THEIR METHYL DERIVATIVES

Aromate (position)	δ (ar H)* ppm	Alkene, vinylsulfide or vinylether	δ (vinyl H)‡ ppm	Δδ§ ppm	Ref.
benzene	7·37	cyclohexene	5·59	1·78	40
thiophene (α)	7·30	2,3-dihydrothiophene (α)	6·12	1·18	41
thiophene (β)	7·10	2,3-dihydrothiophene (β)	5·53	1·57	
furan (α)	7·42	2,3-dihydrofuran (α)	6·23	1·19	42
furan (β)	6·37	2,3-dihydrofuran (β)	4·86	1·51	
	δ (CH_3)†		δ (CH_3)		
toluene	2·32	1-methylcyclohexanes	1·52	0·80	43
2-methylthiophene	2·50	$H_2C{=}C(CH_3){-}S{-}$	1·86	0·64	44
3-methylthiophene	2·28	dipropenylsulfide	1·72	0·56	45
2-methylfuran	2·29	methylisopropenylether	1·74	0·55	46
		α-methylpyranes			47
3-methylfuran	2·04	dipropenylether	1·60	0·44	45
		1-methoxy-2-methyl-cyclohexanes			48

* These δ values were taken from Ref. 24.

† The δ value of toluene was taken from Ref. 24; the other δ values were determined in CCl_4 and extrapolated to infinite dilution by Drs. S. van der Werf, who also synthesized these methylaromatics.

‡ The spectra, apart from those taken from the literature, were taken from about 10% solutions of the compounds in CCl_4 with a Varian A–60. The δ values correspond to the center of a multiplet.

§ Δδ = δ (ar H) − δ (vinyl H), which is a measure for the deshielding of the aromatic or methyl protons.

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[39] J. H. Goldstein and G. S. Reddy, *J. Chem. Phys.* **36**, 2644 (1962).

[40] K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.* **83**, 1226 (1961).

[41] This compound was prepared in our laboratory by H. Wynberg and J. W. van Reijendam according to S. F. Birch and D. T. McAllan, *J. Chem. Soc.* 2556 (1951).

[42] Ref. 3, p. 62.

[43] G. V. Smith and P. J. Trotter, *J. Org. Chem.* **28**, 2450 (1963).

[44] Because NMR spectral data of this grouping are not recorded, we have obtained the δ (CH_3) by valuation as follows. The difference between the δ (CH_3) of isopropenylethers and propenylethers is 0·14 ppm (Table 6). This difference is added to the δ (CH_3) of dipropenylsulfide, giving a δ (CH_3) of 1·86 ppm for an isopropenylsulfide. This procedure is not entirely correct but probably gives the best value in this case.

[45] We are grateful to Dr. L. Brandsma (University of Utrecht) for sending us samples of these compounds. The methyl protons of dipropenylether showed δ 1·58 ppm.

[46] G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.* **38**, 2736 (1963).

[47] A. Hinnen and J. Dreux, *Bull. Soc. Chim. Fr.* 1492 (1964). Moreover, the methyl protons in 2,6-dimethyl-4,4-dipropyl-γ-pyran, prepared in our laboratory by B. Zwanenburg and J. A. van Zorge showed δ 1·75 ppm.

[48] M. F. Ansell, J. W. Lown, D. W. Turner and D. A. Wilson, *J. Chem. Soc.* 3036 (1963).

and furan relative to benzene from the deshielding values of protons or methyl group protons attached to the aromatic ring. These deshielding values were determined by comparing the δ values of the aromatic protons with the δ values of vinylic protons of related olefinic compounds in which no ring current can take place (Table 6). These non-aromatic olefinic compounds are not chosen in an entirely correct manner. The absolute deshielding value of benzene ($\Delta\delta$ 1·50) is generally obtained by comparing its protons with those of 1,3-cyclohexadiene, cyclooctatriene and cyclooctatraene.[9,22] However, the olefinic compounds related to thiophene and furan should then contain a butadien-1-yl sulfide or a butadien-1-yl ether grouping. As NMR spectra of these groupings are not available, we have taken mono alkenes and unconjugated vinylsulfides and vinylethers as non-aromatic compounds related to benzene, thiophene and furan. Indeed, we then obtain too high deshielding values in every case, but this will not affect the *ratio* of deshielding values appreciably.* Similarly the deshielding values of the methyl groups in toluene, methylthiophene and methylfuran were obtained by comparing their methyl δ values with those of the appropriate monoalkenes and with unconjugated vinylsulfides and vinylethers (Table 6).

TABLE 7. RING CURRENTS IN THIOPHENE AND FURAN RELATIVE TO BENZENE AS CALCULATED FROM THE DESHIELDING VALUES IN TABLE 6

Position in thiophene and furan	Relative ring currents		
	Benzene	Thiophene	Furan
α aromatic H	100	66	67
β	100	88	85
mean (α and β)	100	77	76
α CH_3	100	80	69
β	100	70	55
mean (α and β)	100	75	62

The relative ring currents as determined from the deshielding values differ appreciably for the α and β positions in thiophene and furan (Table 7). Nevertheless the

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* As pointed out by a referee, the difference in ring size between benzene, thiophene and furan might affect the calculated ratio of ring currents in these aromatics. Indeed, the induced ring currents in "perfectly aromatic" rings with the same number of delocalized electrons all are equal, regardless of the ring size ($I = -ne^2H_0/4\pi mc$).[4] However, the mathematical expression of the magnetic field caused by the induced ring currents in benzene contains the radius a (taken as 1·4 Å) in the denominator. An estimation of the radii of thiophene and furan using the molecular parameters given by R. M. Acheson, *An Introduction to the Chemistry of Heterocyclic Compounds* pp. 79 and 104. Interscience, New York, N.Y. (1960) gives values of 1·3 Å for thiophene and 1·2 Å for furan. Therefore, the protons of "perfectly aromatic" thiophene and furan would be predicted to be shifted by an amount of 8–15% more than the protons in benzene because of the difference in ring size. This affects our results in an opposite direction. We have calculated the ring current ratio of benzene, thiophene and furan from their shielding and deshielding values. When we also account for the differences in ring radii, the ring current ratio number of thiophene should be decreased by 8% and of furan by about 15%. However these percentages may be much too large because we have not yet accounted for the fact that the cylindrical coordinates ρ and z are also affected by the ring size, as they are expressed in units of ring radii. In going from benzene to thiophene or furan, the ρ and z coordinates will increase in numerical value. This increases the ring ratio numbers of thiophene and furan again. Consequently, the net effect of the ring size on the ratio numbers will be relatively small.

mean deshielding values agree reasonably well with the shielding values in Table 5. In this respect it is not surprising that the deshielding values for the protons attached to the aromatic ring show less agreement, as these are much more subjected to local diamagnetic shielding by the hetero atoms than the methyl protons are.[35]

EXPERIMENTAL PART

All m.ps and b.ps are uncorrected. The UV spectra were determined in 96% ethanol solution with a Zeiss spectrophotometer, model PMQ II. The IR spectra were determined from KBr discs (unless otherwise stated) with a Perkin-Elmer Infracord, model 137. The micro-analyses were carried out in the Analytical Section of our Department under the direction of Mr. W. M. Hazenberg. Only new components were analysed.

Starting materials†

1,5-*Bis*(2-*thienyl*)*pentadien*-3-*one*.[49] The dienone was prepared from 2-thiophenealdehyde and acetone. As crystallization from ethanol produced tar, the crude material was dissolved in benzene below 40°, treated with active carbon and then crystallized by careful addition of hexane. The yield was 74% (lit. 57·5%) of yellow needles, m.p. 116–117·5° (lit. 113–114°).[49] The UV spectrum showed a maximum at 373 mμ (ε 34800). The IR spectrum showed strong absorptions at 1655 cm^{-1} ($C=O$); 1600 cm^{-1} ($C=C$) and 1555 cm^{-1}.

1,5-*Bis*(2-*furyl*)*pentadien*-3-*one*.[50,51] As the literature procedures gave considerable tar formation, we have improved the preparation as follows: To a solution of 75 g NaOH in 1 l. water and 375 ml ethanol, a mixture of 96 g (1 mole) freshly distilled furfural and 29 g (0·5 mole) acetone was added with stirring and ice cooling. The addition, (45 min), was attended by the formation of a yellow oil, which was induced to crystallize by adding solid CO_2. After stirring for another 45 min at 0°–5°, the yellow precipitate was separated quickly by filtration. Warming up to room temp caused immediate tar formation. The crude product after crystallization from light petroleum (b.p. 40–60°) gave a first crop of 55·6 g (52%) yellow needles, m.p. 59–60° (lit. m.p. 60–61°[50]; 61–62°[51]). The mother liquor, which still contained an appreciable amount of product, was not further worked up. The UV spectrum showed a max at 373 mμ (ε 33500). The IR spectrum showed bands at 1660 cm^{-1} ($C=O$); 1620 cm^{-1} ($C=C$), 1580 cm^{-1} and 1545 cm^{-1}.

3,3-*Dimethyl*-9,9-*dimethylthio*-7,11-*diphenylspiro*[5,5]*undecane*-1,5-*dione* (E). A rapid stream of methanethiol was passed through a solution of 1·015 g (3·0 mmole) of B[1a] in 10 ml acetic acid containing 1·0 ml borontrifluoride ether. Crystallization of the thioketal E was induced by adding 30 ml ethanol, followed by water until a turbidity remained. After one night at 0°, 520 mg (38%) colourless product, m.p. 132–140° was obtained. Four recrystallizations from ethanol gave colourless needles, m.p. 141–142°. The IR spectrum showed a strong carbonyl band at 1670 cm^{-1} and a half as intense peak at 1700 cm^{-1}. (Found: C 71·4, 71·7; H 7·2, 7·3; S 13·6, 13·8; $C_{27}H_{32}O_2S_2$ requires: C 71·63, H 7·13, S 14·17%).

3,3-*Dimethyl*-7,11-*diphenylspiro*[5,5]*undecane*-1,5-*dione* (G). The 9-ethylene thioketal of 3,3-dimethyl-7,11-diphenylspiro[5,5]undecane-1,5,9,-trione was prepared from spirotriketone B and ethane-1,2-dithiol according to the directions described for thioketal E. The product crystallized immediately from the solution in good yield. Two recrystallizations from ethyl acetate gave colourless needles of the 9-ethylene thioketal of spirotriketone B, m.p. 263–264°. (Found: C 71·8, 71·7; H 6·8, 6·7; S 14·1, 14·2; $C_{27}H_{30}O_2S_2$ requires: C 71·95, H 6·71, S 14·23%).

Desulfurization of the 9-ethylene thioketal of triketone B was affected with Raney Ni W5 in dioxan, as described previously for thioketal D.[1a] After 2 recrystallizations from ethanol, the diketone G melted at 145·5–146·5°. The IR spectrum showed a strong carbonyl band at 1690 cm^{-1} and a half as intense a peak at 1720 cm^{-1}. (Found: C 82·9; H 8·0; $C_{25}H_{28}O_2$ requires: C 83·28, H 7·83%).

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† We are grateful to Mr. H. J. M. Sinnige for preparing the starting materials.

[49] R. E. Miller and F. F. Nord, *J. Org. Chem.* **16**, 1728 (1951).

[50] L. Claisen and A. C. Ponder, *Liebigs Ann.* **223**, 146 (1884).

[51] V. F. Lavrushin, S. V. Tsukerman and A. I. Artemenko, *J. Gen. Chem. U.S.S.R.* **31**, 2832 (1961).

[52] *Org. Syntheses* (Edited by A. H. Blatt) Coll. Vol. 2; p. 345. J. Wiley, New York (1950).

2,2-Dibenzylcyclohexane-1,3-diones H and I. Compounds H and I were prepared after the directions given by Stetter and Klauke.[58] Compound H melted at 183·5–185° (lit. 185°[58]). The UV spectrum showed maxima at 253 mμ (ε 412), 259·5 mμ, (ε 480), 265·5 mμ (ε 410) and 292 mμ (ε 158). The mono 2,4-dinitrophenylhydrazone of diketone H melted at 197–199°. (Found: C 65·8, 65·7; H 5·5, 5·1; N 11·9, 11·9; $C_{26}H_{24}N_4O_5$ requires: C 66·09, H 5·12, N 11·86%).

5,5-Dimethyl-2-benzylcyclohexane-1,3-dione was obtained by monobenzylation of dimedone as colourless needles, m.p. 154–155°. The UV spectrum showed a max at 265 mμ (ε 15100). The IR spectrum (nujol suspension) showed a small peak at 1640 cm^{-1} and very strong bands at 2600 cm^{-1} and 1550 cm^{-1} (enol). (Found: C 78·0, 78·4; H 7·9, 7·8; $C_{15}H_{18}O_2$ requires: C 78·23, H 7·88%).

Compound I was obtained by benzylation of 5,5-dimethyl-2-benzylcyclohexane-1,3-dione as colourless needles, m.p. 133·5–134·5. The UV spectrum showed max at 253 mμ (ε 489), 259·5 mμ (ε 503), 266 mμ (ε 401) and 291 mμ (ε 184). The IR spectrum showed a strong carbonyl absorption at 1690 cm^{-1} and a half as intense peak at 1720 cm^{-1}. (Found: C 82·9, 82·8; H 7·6, 7·4; $C_{22}H_{24}O_2$ requires: C 82·46, H 7·55%).

7,11-Bis(2-thienyl)spiro[5,5]*undecane-1,5,9-trione* (J). The double Michael reaction was carried out as previously described for dibenzalacetone as dienone.[14] A solution of 2·99 g (12·2 mmole) of 1,5-bis(2-thienyl)pentadien-3-one and 1·50 g (13·4 mmole) of cyclohexane-1,3-dione (Fluka A. G., Buchs S. G., Switzerland, recrystallized from benzene; m.p. 95–99°) in 10 ml absolute ethanol, containing 2·0 ml of 2% solution of Na in absolute ethanol, was refluxed for 4·5 hr. Crystallization was induced by adding 20 ml ethanol followed by 10 ml water together with a few drops acetic acid for neutralization. After a few hr at room temp, a yellow precipitate was collected and immediately crystallized from 15 ml ethanol. This gave 0·766 g (17·5%) spirotriketone J as yellow needles, m.p. 151–152·5°. Only after one sublimation at 140°/0·01 mm followed by 2 recrystallizations from ethanol, an analytically pure product was obtained as colourless needles, m.p. 151–152·5°. The UV spectrum showed a max at 236 mμ (ε 16500). The IR spectrum showed two carbonyl bands at 1680 and 1705 cm^{-1}. (Found: C 63·2, 63·4; H 5·1, 5·1; S 17·5, 17·6; $C_{19}H_{18}O_3S_2$ requires: C 63·65; H 5·06; S 17·88%).

3,3-Dimethyl-7,11-bis(2-thienyl)spiro[5,5]*undecane-1,5,9-trione* (K). The reaction between 4·19 g (17·0 mmole) of 1,5-bis(2-thienyl)pentadien-3-one with 2·41 g (17·2 mmole) of dimedone (m.p. 143–146°) was carried out as described above for compound J. The brown yellow reaction solution was not diluted, but kept at 0°. After 3 days 1·62 g (25%) of yellow crystals, m.p. 175–181° (dec) were obtained. Two recrystallizations from ethanol gave the spirotriketone K as colourless needles, m.p. 178–181° (dec). The UV spectrum showed a max at 238 mμ (ε 15400). The IR spectrum showed carbonyl bands at 1680 and 1720 cm^{-1}. (Found: C 64·9, 65·2; H 5·8, 5·8; S 16·4, 16·4, $C_{21}H_{22}O_3S_2$ requires: C 65·25; H 5·74; S 16·59%. Mol. wt (determined with a Mechrolab Osmometer, model 301 A, in benzene) Found: 379, 387; calc.: 386·5).

3,3-Dimethyl-9,9-dimethylthio-7,11-bis(2-thienyl)spiro[5,5]*undecane-1,5-dione* (L). The dithienylspirotriketone K was converted into the 9,9-dimethylthioketal as described above for the preparation of thioketal E. The thioketal L was obtained in 70% yield as colourless needles, m.p. 173–174·3° after 2 recrystallizations from ethanol. The IR spectrum exhibited a strong carbonyl band at 1670 cm^{-1} and a half as intense peak at 1700 cm^{-1}. (Found: C 59·6, 59·6; H 6·2, 6·2; S 27·2, 27·2; $C_{23}H_{28}O_2S_4$ requires: C 59·44; H 6·07; S 27·60%).

1,5-Bis(2-furyl)spiro[5,5]*undecane-1,5,9-trione* (M). A solution of 4·27 g (20·0 mmole) 1,5-bis(2-furyl)pentadien-3-one and 2·21 g (19·8 mmole) cyclohexane-1,3-dione in 10 ml absolute ethanol containing 2·0 ml of 2% solution of Na in absolute ethanol was refluxed for 1 hr. The solution was diluted with 30 ml ethanol and kept at 0° during one night. There were obtained 1·30 g (20%) brown yellow crystals, m.p. 140–148°. Two recrystallizations from ethanol, in which it is slightly soluble, raised the m.p. to 155–157°. The UV spectrum showed a max at 216 mμ (ε14700). The IR spectrum showed carbonyl absorptions at 1740 and 1695 cm^{-1}. (Found: C 69·8, 69·9; H 5·7, 5·7; $C_{19}H_{18}O_5$ requires: C 69·9; H 5·56).

3,3-Dimethyl-7,11-bis(2-furyl)spiro[5,5]*undecane-1,5,9-trione* (N). The reaction between 2·80 g (13·1 mmole) 1,5-bis (2-furyl) pentadien-3-one and 1·85 g (13·2 mmole) dimedone was carried out as described for compound M. The product crystallized already from the boiling reaction solution. There were obtained 0·950 g(27%) colourless needles, m.p. 190–200° (dec). Two recrystallizations from ethanol, in which it is very slightly soluble, raised the m.p. to 198–201° (dec). The UV spectrum showed a max at 220 mμ (ε 14600). The IR spectrum showed carbonyl bands at 1670 and

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1700 cm^{-1}. (Found: C 70·9, 71·1; H 6·4, 6·5; $C_{21}H_{22}O_5$ requires: C 71·17, H 6·26%. Mol. wt (determined with a Mechrolab osmometer, model 301 A, in benzene) Found: 343, 346; calc. 354·4).

2,2-Dimethylcyclohexane-1,3-*diones* R *and* S. Diketone R was prepared after Eskola *et al.*[54] and melted at 35·0–36·5° (reported 35·5–36·0). Diketone S was prepared after Halsall and Thomas[55] m.p. 94·5–95·0° (reported 98°).

Deuteration of the diarylspirotriketones B *and* K. The deuteroethanol, used in the deuteration, was prepared by hydrolysis of ethyl orthoformate with deuterium oxide[56] and had b.p. 77·5–80·0°. The NMR spectrum showed a total absence of the hydroxylic proton absorption.

Deuteration of compound B. A solution of 862 mg B (m.p. 131–132·0°) in 8 ml deuterated ethanol containing about 10 mg Na was refluxed for 16 hr, while moisture was excluded. After neutralization with a few drops acetic acid, dissolved in deuterated ethanol, the solution was concentrated to 4 ml. Keeping the solution one night at 0° gave 125 mg colourless deuterated product, m.p. 130·5–132·0° after one crystallization from ethanol.

The same experiment, when performed at room temp during 16 hr, gave no detectable deuteration.

Deuteration of compound K. A solution of 403 mg K (m.p. 177–180°, dec) in 11 ml deuterated ethanol, containing about 10 mg Na, was refluxed for 15 hr. The solution was neutralized as before and concentrated to 3 ml. After one day at −20°, only 27 mg colourless deuterated product was obtained, m.p. 174–177° (dec).

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