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THEORETICAL STUDY ON THE OPTICAL ACTIVITY OF SPIRO[3.3]HEPTA-1,5-DIENE

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Abstract—The spectroscopic and chiroptical properties of the title compound **1** has been predicted and interpreted by a quantum mechanical approach using the CNDO–CI modification of Del Bene and Jaffé. The calculated rotational strength of the longest wavelength transitions according to the method of Hug and Wagnière suggests left-handed chirality for levorotatory **1**. The assignment is in agreement with previous work. In addition, the same computational method has been employed for spiro[4.4]nona-1,6-diene (**2**) and spiro[4.4]nonatetraene (**3**).

The UV and CD spectra of compounds containing π electrons have been of great interest to spectroscopists and theoretical chemists. In recent years several synthetic examples of unsaturated dissymmetric spiranes have been described[1-3] of which one theoretical study gave rise to an assignment of absolute configuration.[4] Two calculations† have been reported on the chirality of spiranes. Our current interest in the spectroscopic and chiroptical properties of the title compound **1**[6] and a recent approch to the chirality of spiro[4.4]nona-1,6-diene (**2**)[1,4] prompted us to scrutinize the surprising discrepancy in absolute configuration assignment to both spirodiene **1** and **2**. From the different kinds of approaches[7] we chose the concept of a semiempirical wave mechanical computation of rotational strength for both spirenes. As a proper MO model for the diagnosis of the relative position of the electric and magnetic transition moments, the CNDO–CI method was preferred. The original CNDO/2 program[9] was compared with a modified version of Del Bene and Jaffé[10] concerning the reproduction of the experimental results with the electronic spectra of π-systems **1**, **2** and **3**.

In Table 1 the parameter values according to the original CNDO/2 version[9] (method A), the Del Bene and Jaffé modification[10] (method B) and the CNDO formalism of Hug and Wagnière[4] (method C) are listed. The results of both latter calculations are compiled in Table 2. The data of method A have been left out. This original CNDO/2 method was devised for ground state properties, not for excited states or transitions. From the results of the various computational approaches in Table 2 we may conclude that the spectroscopic data are predicted most accurately by the modified CNDO/2 approximation proposed by Del Bene and Jaffé.[20] This inference is in agreement with theoretical predictions for a wide variety of compounds containing π-electronic systems.[10] For the oscillator and rotational strengths calculations (*vide infra*) this approximation was in fact used.

The optical activity of spirodienes **1** and **2** having C_2 symmetry can be described as the result of the interaction between both equivalent chromophoric parts of these molecules under the influence of light.[4] It has been shown[4] that a similar pattern for the long-wavelength part of the CD spectrum of this kind of compounds is predicted in the exciton model[18] as well as with the inherently dissymmetrical concept. The same tendency is observed in the particular systems **1** and **2**. Both approaches result in a positive Cotton effect of the longest

Table 1. Parameterization (values in eV)[a]

	$\beta_A^{o\,b}$		γ_{AA}^{c}	
	H	C	H	C
method A	−9	−21	20·40	16·06
method B	−12	−17	12·85	11·11
method C	−13·6	−20·0	12·85	10·21

[a] N.B. β_{AB} and γ_{AB} are differently defined by Hug and Wagnière.

[b] β_A^o: emperically determined resonance integral terms.

[c] γ_{AA}: one-center coulomb integrals.

[d] This value indicates $\beta(2s, 2s)$; $\beta(2p, 2p) = -10{\cdot}91$.

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†Two tentative determinations of the absolute configuration of spiranes whose optical activity is due only to the substitution pattern have to be mentioned. W. Kuhn and K. Bein, [*Z. Phys. Chem.* Abt. B, **24**, 335 (1934)], calculated the S configuration for *d*-dipyruvic erythritol and T. M. Lowry and W. C. G. Baldwin [Proc. Roy. Soc. *A162*, 204 (1937), assigned the S configuration to *l*-spiro-[3.3]heptane-2,6-diamine. See also reference 5.

Table 2. Singlet–singlet transitions in spirenes **1**, **2** and **3** (values in nm)[a]

	Method B	IP[b]	Method C[m]	IP[b]	UV (exp.)	PES (exp.)
1	[189·8(B); 182·5(A)]	10·34	[158·5(B); 157·9(A)]	11·84	~200[h]	9·02[i]
	200·4(B); 193·1(A)[c]	(9·68)	187·5(B); 187·7(A)[g]			
2	[193·5(B); 183·7(A)][d]	10·15	— —	—	198[j]	—
	204·5(B); 192·8(A)[cd]		185·4(B); 181·0(A)[dg]			
3	[264·1 ; 192·2][e]	9·33	— —		276; 218[k]	—
	273·5 ; 205·4[ef]	(8·84)	— —			7·99[l]

[a] Models were constructed having C_2 and S_4 symmetry and the geometry of cyclobutene[11], cyclopentene[12] and cyclopentadiene[13], respectively; values without CI brackets, symmetry of transition in parentheses.

[b] First ionization potential (in eV), calculated according to equation $IP = -\epsilon$ and/or $IP = -[E(mol) - E(mol^{+})]$; the latter one quoted in parentheses.

[c] Four π–π^* configurations; if 6 HOMO and 6 LUMO States were mixed, the following values were obtained for compound **1**: 206·6(b), 197·2(A).

[d] Planar model.

[e] Degenerate.

[f] 36 Configurations.

[g] 120 Configurations.

[h] Ref. 6, [i] Ref 15, [j] Ref 1a, [k] Ref 14, [l] Ref 24.

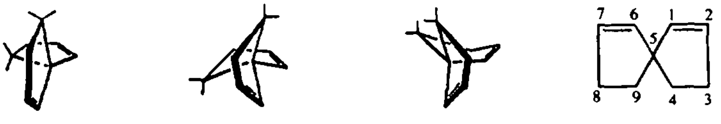
[m] These calculations were kindly carried out by Prof. Wagnière.

wavelength transition with B symmetry followed by a negative one of a transition with A symmetry for the planar models of **1** and **2** with a righthanded sense of screw (Fig 1). Even for the nonplanar conformers of **2** (*vide infra*) the mutual opposite pattern can be explained in both ways. We tend to view the homoconjugated 1,4 spirolinked diene systems as an inherently dissymmetric chromophore because a considerable spiroconjugation has been observed for diene **1**[6a] and because an indication has been obtained for a non-planar **1**.[6a] This latter additional feature of a distorted molecule may be explained as an endeavour of **1** to diminish the importance of a destabilizing spiroconjugative interaction.[19]

In order to get quantitative data concerning the optical activity and to determine the absolute configuration of spirenes **1** and **2**, the rotational strength of the transitions in the near-UV were computed by application of generally developed standard quantum mechanical methods.[4,22] In contrast to study of Hug and Wagnière[4] the eigenvectors of Del Bene and Jaffé's modification (*vide supra*) were used. Following a producedure of Hug and Wagnière,[4] expressions for the integrals involving the operator $\vec{\nabla}$ and $\vec{r} \times \vec{\nabla}$ were evaluated and the rotational and dipole strengths were calculated. Not only the transition energies (*vide supra*) but also the rotational strength, dipole strength and oscillator strength[16] were then refined by a configuration interaction calculation. A detailed description of CI and its mathematical formulation has been given by Pariser.[23] In this work, CI was restricted mostly to the four π–π^* excitations and to a maximum quantity of 49 lowest singly excited states due to the limited amount of computer storage. In the former case the influence on the rotational strength dependent on the amount of CI was verified and it was found[17] that the applied degree of mixing states was a justified selection. In Table 3 the calculations are summarized and compared with experiment. It is to be noted that for spirene **2** two additional puckered conformers are distinguished based upon model studies and on the geometry of cyclopentene. In Fig 2 both conformers having cyclopen-

1 **2** **3**

Fig 1. R or 4S - spiro[3.3]hepta - 1,5 - diene (**1**), R or 5S - spiro[4.4]nona - 1,6 - diene (**2**) according to the old and new method of the Cahn, Ingold, Prelog convention,[8] respectively, and spiro[4.4]nonatetraene (**3**).



2a **2b** **2c**

Fig 2. Geometrical isomers of R (or 5S) spiro[4.4]nona - 1,6 - diene planar **2a** and puckered **2b** and **2c**; α = 180°, 208·8° and 151·2°, respectively.

Table 3. Comparison of experimental and calculated rotational strengths (R),[a] dipole strengths (D)[b] and oscillator strengths (f)

	λ^c (calc)	R (calc)	D (calc)	D^d (exp)	f (calc)	f^e (exp)	$\Delta\epsilon^f$ (calc)
1	200·4	−77·20	8·40	8·56	0·197	0·155	−25·3
	193·1	+82·85	1·98	—	0·048	—	+26·2
2a	204·5	−26·01	11·68	14·90	0·268	0·259	−8·7
	192·8	+29·51	0·26	—	0·006	—	+9·3
2b	208·1	−58·92	10·51	14·90	0·237	0·259	−20·1
	192·3	+52·59	1·46	—	0·036	—	+16·5
2c	204·9	+25·36	11·68	14·90	0·268	0·259	+8·5
	196·8	−10·26	0·02	—	0·001	—	−3·3
3	273·5[g]	0	1·59	0·90	0·054	0·024	0
	205·4	0	2·73	6·36	0·063	0·115	0

[a]In units of Biot. [b]In units of Debye.[2c] In nm.

[d]Calculated according to the equation $D \simeq 0{\cdot}92 \times 10^{-38}\sqrt{\pi}.\Delta/\lambda o.\epsilon_{max}$, where Δ is half of the bandwidth at $\epsilon = \epsilon_{max}/E$ and is assumed to be 15 nm and λo is the wavelength at ϵ_{max}.

[e]Calculated according to the expression $f = 4{\cdot}32 \times 10^{-9} \times \epsilon_{max} \times \Delta\nu\tfrac{1}{2}$, where $\Delta\nu\tfrac{1}{2}$ is the half-width of the absorption band and is assumed to be appr. 5000 cm^{-1}.

[f]Calculated according to the equation $R \simeq 0{\cdot}23 \times 10^{-38}.\sqrt{\pi}.\Delta/\lambda o.\Delta\epsilon_{max}$,

[g]Degenerate.

Table 4. Results CNDO/2 calculations[a] on spirodienes **2a**, **2b** and **2c**

	E total (eV)	E el. (eV)	E n.r. (eV)
2a	0	0	0
2b	0·272	−16·00	16·28
2c	0·274	−11·08	11·36

[a]Method A.

tene geometry[12] and C_2 symmetry are represented only differing in the dihedral angle (α) of the planes C1, C2, C3, C5 and C3, C4, C5.

From Table 3 it is seen that the present work does not give conclusive evidence for assignment of absolute configuration to **2**, if conformational mobility is assumed. Conformational analysis by means of this CNDO formalism (Table 4) suggests a situation which is intelligible in terms of a non-rigid system **2** containing predominantly the planar conformation. The probable equilibrium should lie substantially toward the planar form with the conformers **2b** and **2c** as the most puckered extremes. Contrary to this procedure Hug and Wagnière[4] were able to assign the R or 5S configuration to *planar* **2** for which a positive resultant of superposed Cotton effects was calculated. On the other hand, according to the present calculation the R or 4S to levororatory spirodiene **1** is assigned, even if a Gaussian line shape analysis is performed. This assignment is in agreement with previous work.[6b]

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