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Circular Dichroism Due to Exciton Coupling between Two 1-Aryltriazene Chromophores

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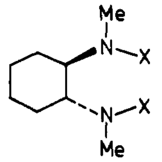
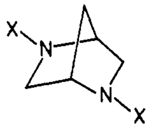
The exciton chirality method is a powerful tool in stereochemical studies of natural and synthetic organic compounds.[1] Two identical or similar chromophores undergoing strong electronic transitions interact with each other to exhibit two intense Cotton effects (CEs) of opposite signs and comparable intensities. The CE signs are determined by the helicity of two electric transition moments, so the absolute configuration can be readily assigned. The method is widely applied to compounds bearing two or more hydroxyl groups, which may be derivatized with benzoate type chromophores.[1,2] Similarly diamino systems can be transformed into dibenzamides,[3] bis-*p*-methoxycinnamides,[4] bis-2,4-dinitrophenyl derivatives,[5] or biscyanine dyes.[4]

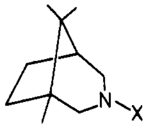
This paper reports the exciton coupling in the CD spectra of bis(1-aryl)triazenes **1**, **2**, **4**, and **5** derived from optically active diamines, and stereochemical predictions based on analogous dibenzamides **3** and **6** are discussed. For comparison monotriazenes **7** and **8** were prepared and their spectra recorded.



1, X: N=N-Ph
2, X: N=N-p-C_6H_4-NO_2
3, X: PhCO



4, X: N=N-Ph
5, X: N=N-p-C_6H_4-NO_2
6, X: PhCO

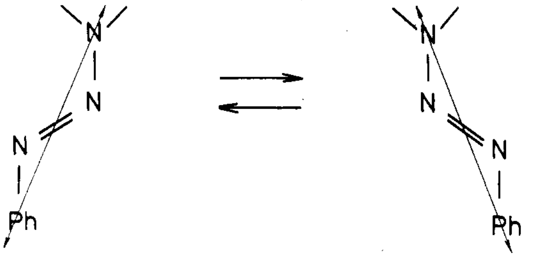


7, X: N=N-Ph
8, X: N=N-p-$C_6H_4NO_2$

Results and Discussion

The UV spectrum of **7** contains three absorption bands, where the intense long-wavelength band appearing at 306 nm (ϵ 15 800) in cyclohexane and at 308 nm in methanol can be associated with the π-π^* transition of origin similar to that observed in other azo compounds.[6,7] The two remaining bands at ca. 290 and 225 nm, both with marked fine structure, correspond probably to the ^1L_b and ^1L_a aromatic transitions, respectively. The *p*-nitro substituent in **8** shifts the long-wavelength absorption to 360 nm. The CD spectra of **7** and **8** (Table I) show only very weak CEs corresponding to the lowest energy π-π^* excitation. This behavior of monotriazenes contrasts with that of bistriazenes **1**, **2**, **4**, and **5**, which due to exciton coupling between the chromophores, exhibit strong bisignate CEs in the region of the first π-π^* absorption. The CEs associated with the higher energy transitions are rather weak.

The polarization of the long-wavelength excitation was assigned from the CNDO/S-CI calculations for the 1-phenyltriazene (PhN=NNH$_2$) molecule.[8] The electric transition moment is directed from the phenyl ring to the N-3 atom and makes an angle of 49° with the N=N bond. The 1-aryltriazene moiety itself is approximately planar, and the trans configuration of the azo group is favored according to the X-ray diffraction studies.[9,10] It should be noted that the rotation about the N2–N3 bond though hindered, due to its partial double character, is fast at room temperature as the NMR investigations showed.[10,11] Thus the transition moment can be considered as directed along this bond on average in time.



The sequence of a positive CE at the longer wavelengths and a negative one at the shorter wavelengths (positive exciton coupling) in the CD spectra of **1** and **2** (Figure 1) implies the right-handed screwness of the transition moments. The most preferred conformation of **1**, calculated by molecular mechanics method (MM2),[12,13] reveals the *clockwise* twist of the two chromophores (the angle between the triazene transition moments is of 55°) (Figure 2) and governs the CE signs. It is noteworthy that the

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(13) The original Allinger's MM2 parameterization[12] was extended to triazenes by taking a part of parameters from the set used for azoalkanes (Kao, J.; Leister, D. *J. Am. Chem. Soc.* **1988**, *110*, 7286) and the remaining from the MMX program (Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. *Advances in Molecular Modeling*; Liotta, D., Ed.; JAI Press: Greenwich, 1990; Vol. 2, p 65).

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Table I. Electronic Absorption (UV) and Circular Dichroism (CD) Data of Compounds 1–8

compd	solv[a]	UV λ, nm (ε)	CD λ, nm (Δε)
1	M	306 (24 500)	322 (10.66), 268 (−12.03)
2	M	358 (39 200)	380 (12.01), 338 (−9.31)
3	M	217 (16 500)[b]	235 (12.95)
	CD	218 (17 300)[b]	236 (5.19), 217 (−1.15)
4	M	310 (30 000)	327 (−11.79), 272 (8.25)
5	M	365 (46 700)	376 (−33.95), 332 (18.14)
6	M	217 (19 100)	251 (2.13), 216 (−13.14)
7	C	308 (15 500)	320 (0.86)
8	C	358 (31 200)	355 (0.85)

[a] M = methanol, C = cyclohexane, CD = cyclohexane–dioxane (9:1). [b] Shoulder.

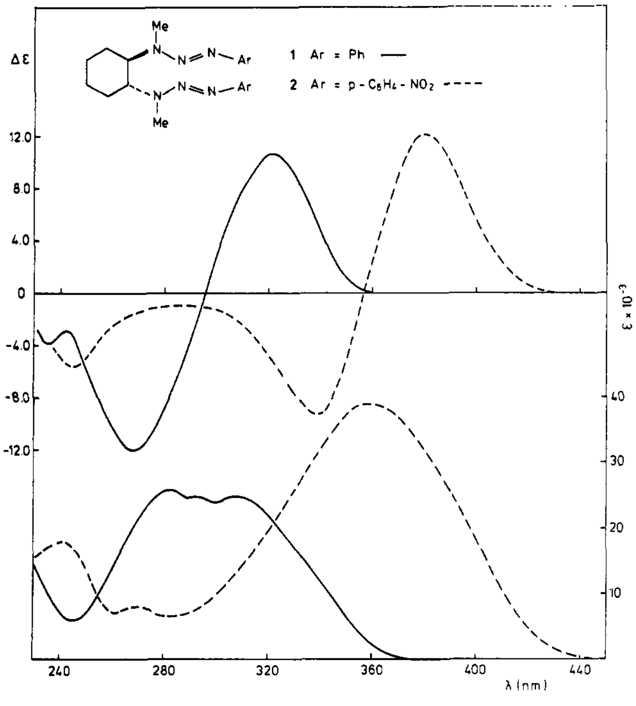


Figure 1. CD and UV spectra of 1 and 2 in methanol.

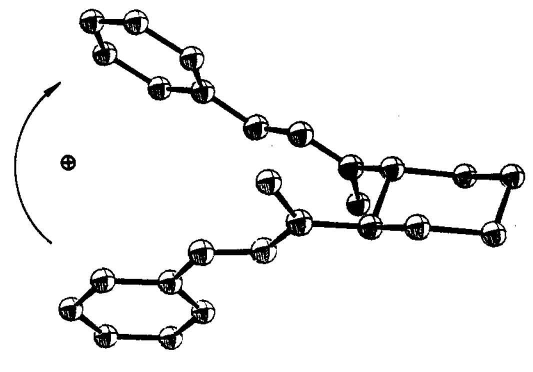
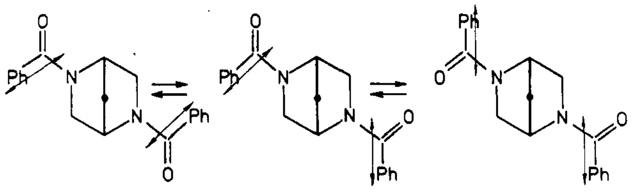


Figure 2. A perspective view of the preferred conformation of 1 calculated by the molecular mechanics (MM2).

mutual orientation of the chromophores in 1 and 2 has an opposite chirality to that of the diamino system. The above situation closely resembles that recently reported by Nakanishi and co-workers[4] for biscyanine dye derived from *trans*-1,2-diaminocyclohexane, which exhibits a bisignate CD of the sign opposite to that expected from the geometry of the diamino system. The *counterclockwise* screwness of the two chromophores in 4 and 5 (the angle between the transitions moments is of 50°) is responsible for the negative exciton coupling in the CD spectra.

The configurational predictions based on the CD of dibenzamides 3 and 6 are rather difficult. In the first case only a single CE is observed at 235 nm in methanolic solution. Whereas 6, though showing a bisignate CE, is, according to the NMR spectra, a mixture of conformers in solution owing to hindered rotation about the amide C–N bond. Thus three different orientations of the two benzamide transition moments contribute to the CE. Both these examples illustrate problems, which may arise when one applies the dibenzoate chirality rule[1] to tertiary amides. However, the rule works well with secondary amides, where the *trans*-amide bond is preferred (cf. *trans*-1,2-dibenzamidocyclohexane showing a strong bisignate CE, which signs conform with the rule[3]), and then the transition polarization is parallel to the C–N bond. There are no problems with assigning of mutual orientation of the transition moments in bis(1-aryl)triazenes. This taken together with the simplicity of their preparation procedure[14] makes them useful derivatives for stereochemical predictions.



Experimental Section

All melting points are uncorrected. CD spectra were recorded on a JASCO J-20 spectropolarimeter. UV measurements were performed on a Beckman 3600 spectrophotometer. ^1H and ^{13}C spectra were obtained with a Bruker MSL-300 spectrometer operating at 300 and 50 MHz, respectively. The restricted rotation about the N–N bond is responsible for split of some signals in the ^{13}C NMR spectra of 7 and 8. Analogously the restricted rotation about the amide C–N bond causes line broadening and the presence of signals corresponding to three conformers in the NMR spectra of 6. IR absorptions were taken with a Zeiss UR-10 spectrometer. The triazenes 1, 2, 4, 5, 7, and 8 were obtained by coupling the diazonium salts of the appropriate aromatic amines with secondary amines.[14] A typical preparation is described for 1.

(1*R*,2*R*)-1,2-Bis[(*N*-methyl-*N*-(phenylazo)amino]cyclohexane (1). To a solution of aniline (1.52 g, 11 mmol) in 5 N hydrochloric acid (5 mL) and $NaNO_2$ (0.76 g, 11 mmol) in water (3 mL) was added dropwise with stirring at 0 °C. To the resulted diazonium salt the solution of (1*R*,2*R*)-1,2-bis(methylamino)cyclohexane dihydrochloride[15] (1.10 g, 5 mmol) in water (5 mL) and aqueous Na_2CO_3 were added until pH 9. The reaction mixture was then stirred for 20 min at 10 °C. The product was extracted with benzene (25 mL), dried ($MgSO_4$), evaporated, and crystallized from methanol: yield 1.14 g (65%); mp 69–70 °C; $[\alpha]^{22}{}_D$ +43.6° (*c* 2.2, C_6H_6); ^1H NMR ($CDCl_3$) δ 7.40–7.11 (complex m, 10 H, Ph), 4.13 (m, 2 H, CHN), 3.12 (s, 6 H, NMe), 2.17–1.42 (complex m, 8 H); ^{13}C NMR ($CDCl_3$) δ 150.93, 128.70, 125.31, 120.56, 66.55, 32.94, 31.37, 25.06; UV (MeOH) λ_{max} 306 nm (ε 24 500), 282 (26 200), 224 (19 900).

Anal. Calcd for $C_{20}H_{26}N_6$ (350): C, 68.54; H, 7.48; N, 23.98. Found: C, 68.56; H, 7.39; N, 24.13.

(1*R*,2*R*)-1,2-Bis[*N*-methyl-*N*-[(4-nitrophenyl)azo]amino]cyclohexane (2) was obtained from *p*-nitroaniline and (1*R*,2*R*)-1,2-bis(methylamino)cyclohexane:[15] mp 165 °C (toluene–hexane); $[\alpha]^{20}{}_D$ +403° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 8.14 (m, 4 H, Ar), 7.39 (m, 4 H, Ar), 4.21 (m, 2 H, CHN), 3.16 (s, 6 H, NMe), 2.23–

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1.46 (complex m, 8 H); ^{13}C NMR (CDCl$_3$) δ 155.63, 144.74, 124.72, 120.60, 67.08, 33.32, 31.06, 24.78; UV (MeOH) λ_{max} 358 nm (ϵ 39 200), 270 (8300), 238 (17 400).

Anal. Calcd for $C_{20}H_{24}N_8O_4$ (440): C, 54.54; H, 5.49; N, 25.44. Found: C, 54.60; H, 5.44; N, 25.47.

(1*R*,2*R*)-1,2-Bis(*N*-methylbenzamido)cyclohexane (3) was obtained by dibenzoylation of (1*R*,2*R*)-1,2-bis(methylamino)-cyclohexane:[15] mp 203–204 °C (toluene–hexane); $[\alpha]^{22}_D$ +122.7° (*c* 1.5, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 7.37 (s, 10 H, Ph), 4.90 (m, 2 H, CHN), 3.06 (s, 0.8 H, NMe), 2.93 (s, 5.2 H, NMe), 1.96–1.44 (complex m, 8 H); ^{13}C NMR (CDCl$_3$) δ 171.64 (CO), 136.75, 129.40, 128.29, 126.65, 58.59, 52.21, 32.33, 29.14, 24.98; IR (CCl$_4$) 1640 (CO), 1405 cm^{-1}.

Anal. Calcd for $C_{22}H_{26}N_2O_2$ (350): C, 75.40; H, 7.48; N, 7.99. Found: C 75.53; H, 7.34; N, 7.84.

(1*S*,4*S*)-2,5-Bis(phenylazo)-2,5-diazabicyclo[2.2.1]heptane (4) was obtained from aniline and (1*S*,4*S*)-2,5-diazabicyclo-[2.2.1]heptane:[16] mp 151 °C (toluene–hexane); $[\alpha]^{22}_D$ −370° (*c* 1.7, C$_6$H$_6$); ^{1}H NMR (CDCl$_3$) δ 7.46–7.18 (complex m, 10 H, Ph), 5.02 (d, *J* = 1.6 Hz, 2 H, H-1 + H-4), 3.96 (d, *J* = 11.9 Hz, 2 H, H-3 + H-6), 3.85 (dd, *J* = 1.9 and 11.9 Hz, 2 H, H-3′ + H-6′), 2.15 (s, 2 H, H-7); ^{13}C NMR (CDCl$_3$) δ 150.28, 128.81, 126.21, 120.63, 61.16, 55.07, 36.16; UV (MeOH) λ_{max} 310 nm (ϵ 30 000), 296 (29 100), 225 (20 500).

Anal. Calcd for $C_{17}H_{18}N_6$ (306): C, 66.65; H, 5.92; N, 27.43. Found: C, 66.93; H, 5.69; N, 27.43.

(1*S*,4*S*)-2,5-Bis[(4-nitrophenyl)azo]-2,5-diazabicyclo[2.2.1]-heptane (5) was obtained from *p*-nitroaniline and (1*S*,4*S*)-2,5-diazabicyclo[2.2.1]heptane:[16] mp 178 °C (toluene); $[\alpha]^{22}_D$ −708° (*c* 1, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 8.19 (m, 4 H, ArH), 7.50 (m, 4 H, ArH), 5.14 (br, 2 H, H-1 + H-4), 4.02 (d, *J* = 12.2 Hz, 2 H, H-3 + H-6), 3.93 (br m, 2 H, H-3′ + H-6′), 2.30 (s, 2 H, H-7); ^{13}C NMR (CDCl$_3$) δ 155.07, 145.34, 124.81, 120.91, 62.11, 55.37, 36.82; UV (MeOH) λ_{max} 365 nm (ϵ 46 700), 273 sh (8600), 223 (17 500).

Anal. Calcd for $C_{17}H_{16}N_8O_4$ (396): C, 51.51; H, 4.07; N, 28.27. Found: C, 51.22; H, 3.93; N, 28.17.

(1*S*,4*S*)-2,5-Dibenzoyl-2,5-diazabicyclo[2.2.1]heptane (6) was obtained by dibenzoylation of (1*S*,4*S*)-2,5-diazabicyclo[2.2.1]-heptane:[16] mp 162 °C (toluene); $[\alpha]^{20}_D$ −32.4° (*c* 2, CHCl$_3$); ^{1}H NMR (DMSO-*d*$_6$) δ 7.56–7.44 (m, 10 H, Ph), 4.91 (br s, 0.45 H), 4.80 (br s, 0.3 H), 4.41 (br s, 0.75 H), 1.32 (br s, 0.5 H), 3.69–3.41 (complex m, 4 H, H-3 + H-6), 2.01 (br s, 0.3 H), 1.90 (br s, 0.9 H), 1.85 (br s, 0.8 H); ^{13}C NMR (DMSO-*d*$_6$) δ 168.18 (CO), 136.28, 135.82, 130.47, 130.15, 128.60, 128.44, 127.57, 127.28, 60.11, 59.15, 57.10, 56.58, 56.33, 55.68, 54.05, 52.86, 38.12, 36.44; IR (CCl$_4$) 1650 (CO), 1415 cm^{-1}; UV (MeOH) λ_{max} 217 nm (ϵ 19 100).

Anal. Calcd for $C_{19}H_{18}N_2O_2$ (306): C, 74.49; H, 5.92; N, 9.14. Found: C, 74.40; H, 5.72; N, 9.11.

(1*S*,5*S*)-1,8,8-Trimethyl-3-(phenylazo)-3-azabicyclo[3.2.1]-octane (7) was obtained from aniline and camphidine:[17] mp 98–99 °C (hexane); $[\alpha]^{22}_D$ +80.4° (*c* 2.2, C$_6$H$_6$); ^{1}H NMR (DMSO-*d*$_6$) δ 7.44–7.20 (m, 5 H, Ph), 4.26 (br d, 0.5 H), 4.06 (br d, 0.5 H), 3.95 (br m, 1 H), 3.71 (s, 1 H), 3.30 (br d, 0.5 H), 3.05 (br d, 0.5 H), 2.00–1.30 (complex m, 5 H), 1.08 (s, 3 H, Me), 1.01 (s, 6 H, Me); ^{13}C NMR (DMSO-*d*$_6$) 150.56, 128.93, 125.36, 120.30, 61.14, 55.10, 54.77, 48.93, 44.18, 41.85, 35.19, 34.19, 26.55, 25.68, 23.56, 17.94; UV (cyclohexane) λ_{max} 306 nm (ϵ 15 750), 296 (16 000), 226 (10 400); UV (MeOH) λ_{max} 308 nm (ϵ 15 500), 294 (15 500), 226 (9300).

Anal. Calcd for $C_{16}H_{23}N_3$ (257): C, 74.67; H, 9.01; N, 16.33. Found: C, 74.91; H, 9.19; N, 16.54.

(1*S*,4*S*)-1,8,8-Trimethyl-3-[(4-nitrophenyl)azo]-3-azabicyclo[3.2.1]octane (8) was obtained from *p*-nitroaniline and camphidine:[17] mp 150 °C (hexane); $[\alpha]^{22}_D$ +92.5° (*c* 1.4, C$_6$H$_6$); ^{1}H NMR (CDCl$_3$) δ 8.19 (m, 2 H, ArH), 7.50 (m, 2 H, ArH), 4.39 (dd, *J* = 15.2 Hz, 0.5 H), 4.17 (d, *J* = 14.7 Hz, 0.5 H), 4.00–3.89 (m, 1 H), 3.71 (s, 1 H), 3.34 (d, *J* = 14.7 Hz, 0.5 H), 2.00–1.35 (complex m, 5 H), 1.06 (s, 3 H, Me), 0.97 (s, 6 H, Me); ^{13}C NMR (CDCl$_3$) δ 156.06, 143.50, 124.79, 120.47, 62.22, 56.60, 55.46, 49.77, 44.70, 44.27, 42.48, 42.12, 35.33, 34.40, 26.64, 25.82, 23.62, 23.54, 18.09, 17.90, 17.45; UV (MeOH) λ_{max} 358 nm (ϵ 31 200), 270 (3600), 237 (10 800).

Anal. Calcd for $C_{16}H_{22}N_4O_2$ (302): C, 63.56; H, 7.33; N, 18.53. Found: C, 63.56; H, 7.47; N, 18.56.

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