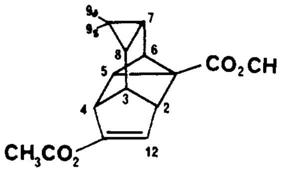
J. Org. Chem. **1986**, *51*, 589–592

mean value for the rotation around the bond C_9–C_{10}]; MS, *m/e* 260, 245, 228, 196, 169, 141, 128. Anal. Calcd for $C_{14}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.08; H, 6.11.

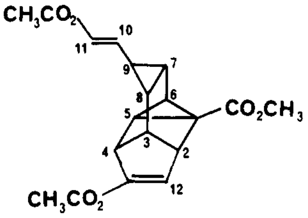
(c) **Adduct 11**:



11

solid, mp > 300 °C; t_R 20.1; IR ($CDCl_3$) 3035, 3020, 1720, 1590 cm^{-1}; NMR (7.42 (d, H-12, $J_{2,12} = 3$), 3.72 (s, OCH_3 on C-13), 3.65 (s, OCH_3 on C-1), 3.12 (dt, H-2, $J_{2,3} = 1.5$, $J_{2,4} = 1.8$), 2.92 (br, H-4, $J_{4,3} = J_{4,5} = 1.5$, $J_{4,6} = 1$), 2.75 (ddd, H-6, $J_{6,7} = 5$, $J_{5,6} = 8$, $J_{6,4} = 1$), 2.16 (dq, H-3, $J_{3,8} = 5.8$, $J_{3,2} = J_{3,4} = J_{3,5} = 1.5$), 1.82 (dt, H-5, $J_{5,6} = 8$, $J_{5,4} = J_{5,3} = 1.5$), 1.23 (m, H-7, $J_{7,8} = J_{7,9a} = 8$, $J_{7,9s} = 4$, $J_{7,6} = 5$), 0.90 (m, H-8, $J_{8,3} = J_{8,7} = 8$, $J_{8,9a} = J_{8,9s} = 4$), 0.52 (dt, H-9a, $J_{9a,8} = J_{9a,7} = 8$, $J_{9a,9s} = 5$), 0.28 (q, H-9s, $J_{9s,9a} = 5$, $J_{9s,7} = J_{9s,8} = 4$); MS, *m/e* 260, 245, 228, 200, 169, 141, 129, 115.

(d) **Adduct 12**:



12

solid, mp > 300 °C; t_R 25.0; IR ($CDCl_3$) 3030, 3000, 1720, 1590 cm^{-1}; NMR (concerning coupling constants, see note for product **10**) 7.41 (d, H-12), 6.42 (dd, H-10), 5.86 (d, H-11), 3.73 and 3.71 (s, OCH_3 on C-11 and C-13), 3.66 (s, OCH_3 on C-1), 3.15 (dt, H-2), 2.98 (br, H-4), 2.81 (ddd, H-6), 2.24 (dq, H-3), 1.91 (dt, H-5), 1.60 (m, H-7, $J_{7,9} = 3$), 1.49 (dt, H-9, $J_{9,10} = 10$, $J_{9,7} = J_{9,8} = 3$), 1.25 (m, H-8, $J_{8,7} = 8$, $J_{8,3} = 5.8$, $J_{8,9} = 3$); MS, *m/e* 344, 277, 252, 237, 225, 193, 165, 152, 128, 115.

5. Reaction with Diethyl Azodicarboxylate. The low- and high-pressure procedures were repeated as above at room temperature with 622 mg (6.77 mmol) of CHT and 555 mg (3.18 mmol) of enophile in CH_2Cl_2 solution (1.5 mL). After reaction, the content of the reaction tube was analyzed by GLC and submitted to the usual workup. The high-pressure runs were shown to contain three compounds which were separated by column chromatography followed by preparative-layer chromatography (with ether–hexane (2:1) as eluent). The first compound was proved to be **16**, diethyl hydrazine-1,2-dicarboxylate (mp 131–132 °C; t_R 12.9; R_f 0.11) by comparison with a commercial sample (Fluka). The other compounds were shown to be the ene adduct **14** already reported[19] (t_R 19.3; R_f 0.36) and the unprecedented norcaradiene adduct **15** (t_R 19.3; R_f 0.29): IR ($CDCl_3$) 3070, 3005, 1730, 1530 cm^{-1}; NMR (numeration as for **9**) 6.23 and 5.97 (t, H-4 and H-5, $J_{4,5} = 8$), 5.20 and 5.12 (br, H-3 and H-6), 4.22 (q, OCH_2), 1.77 and 1.61 (br, H-7 and H-8), 1.26 (t, CH_3), 0.42 (q, H-9a, $J_{9a,9s} = 6$, $J_{9a,7} = J_{9a,8} = 7$), 0.13 (dt, H-9, $J_{9s,9a} = 6$, $J_{9s,8} = J_{9s,7} = 3.5$); MS, *m/e* 266, 176, 93. Anal. Calcd for $C_{13}H_{18}O_4N_2$: C, 58.63; H, 6.81; N, 10.52. Found: C, 58.59; H, 6.74; N, 10.53.

6. Reaction with Dimethyl Mesoxalate. The high-pressure procedure (900 MPa) was repeated with a CH_2Cl_2 solution of 622 mg (6.77 mmol) of CHT and 920 mg (6.29 mmol) of dimethyl mesoxalate at 80 °C during 24 h. The yield of products was 72%. GLC analysis showed the formation of two compounds (95:5). Column chromatography with ether–hexane (2:1) as eluent gave a slightly yellow solid **17** (t_R 16.6; R_f 0.40; mp 76–78 °C): IR (KBr) 3500, 1750, 1620 cm^{-1}; NMR ($CDCl_3$) 6.71 (t, 2 H, C=C), 6.25 (dm, 2 H, C=C), 5.27 (dd, 2 H, C=C), 4.06 (br, 1 H, OH), 3.82 (s, 6 H, OCH_3); MS, *m/e* 238, 220, 147, 119, 91. Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.70; H, 6.17.

Acknowledgment. We thank Dr. A Rahm (University of Bordeaux I) for performing the 1100-MPa run (isomerization attempt of **5**), Dr. R. Breault for linguistic assistance, and E. Schleiffer for GC analyses.

Registry No. **1**, 31456-54-9; **2**, 54382-95-5; *exo*-**3**, 100191-06-8; *endo*-**3**, 31576-25-7; **4**, 5932-77-4; **5**, 100191-07-9; **9**, 100191-08-0; **10**, 100191-09-1; **11**, 100191-10-4; **12**, 100191-11-5; **14**, 100191-12-6; **15**, 100191-13-7; **16**, 4114-28-7; **17**, 100191-14-8; TCNE, 670-54-2; CHT, 544-25-2; 8,8,9,9-tetracyanotricyclo[3.2.2.0^{2,4}]non-6-ene, 16118-23-3; acrylonitrile, 107-13-1; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8; diethyl azodicarboxylate, 1972-28-7; dimethyl mesoxalate, 3298-40-6.

Induction of the Cholesteric Mesophase in Nematic Liquid Crystals: Correlation between the Conformation of Open-Chain Chiral 1,1′-Binaphthyls and Their Twisting Powers

Giovanni Gottarelli* and Gian Piero Spada

Istituto di Scienze Chimiche, Universita' di Bologna, 40127 Bologna, Italy

Richard Bartsch, Guy Solladié,* and Richard Zimmermann

Ecole Nationale Supérieure de Chimie, Universite' Louis Pasteur, 67008 Strasbourg, France

Received November 12, 1985

The twisting powers β_M of 10 optically active open-chain 2,2′-disubstituted 1,1′-binaphthyls of known absolute configuration were measured in biphenyl nematic liquid crystals. The results show that it is possible to correlate the conformation (cisoid or transoid) of the optically active compounds to the sign of their twisting powers: for the absolute configuration *S*, a positive β_M value corresponds to a cisoid conformation while a negative β_M value corresponds to a transoid conformation. These conformational conclusions were in agreement with CD and X-ray data.

Induced cholesteric mesophases are generated by the addition of traces of chiral compounds to nematic liquid crystals.[1-4]

Different substances show a different ability to twist a nematic phase. The twisting power of chiral dopant can

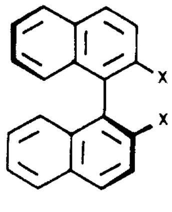
---

(1) Friedel, G. *Ann. Phys. (Paris)* **1922**, *18*, 273–474.

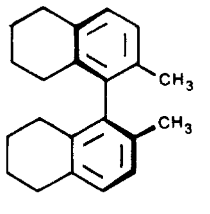
(2) Buckingham, A. D.; Ceasar, G. P.; Dunn, M. B. *Chem. Phys. Lett.* **1969**, *3*, 540.

0022-3263/86/1951-0589$01.50/0

Table I



(I)



(II)

compd	absolute config.	formula	β_M, μm^{-1} [a] K15[b]	E7[b]
1	*S*	I, X = OH	+32	
2	*S*[c]	I, X = CH_2OH	+8.5	
3	*S*	I, X = OCH_2COOH	+4.2[d]	
4	*S*[c]	I, X = NH_2		+2[d]
5	*S*	I, X = OCH_3	+1.5	
6	*S*	I, X = OCH_2Ph	+1.4	
7	*S*[c]	II	+1[d]	
8	*S*	I, X = CH_3		+0.5[d]
9	*S*	I, X = CH_2Br	-4.6[d]	
10	*S*	I, X = $CHBr_2$		-2.4[d]

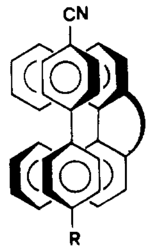
[a] A positive value of β_M corresponds to a right-handed cholesteric (*P*-helix). [b] K15: 4-cyano-4′-*n*-pentylbiphenyl from BDH. E7: a mixture of 4-cyano-4′-*n*-aryl- and 4-cyano-4′-*n*-alkylbiphenyl from BDH. [c] The enantiomer was measured. [d] Not corrected for the optical purity.

be defined as[5,6] $\beta_M = (pcr)^{-1}$, where *p* is the pitch (μm), *c* is the concentration (moles of solute per moles of solution), and *r* is the enantiomeric purity of the dopant.

The twisting power β_M and its sign (+ for a *P*-helix and − for a *M*-helix of the induced cholesteric) characterize the chiral solute in a way similar to the specific optical rotation [α]. However, the physical origin of the two quantities is entirely different. The origin of the optical rotation depends on interactions between light and molecules while the twisting power originates from interactions between molecules of solute and solvent.[6-8,10b]

Quantity β_M, a molecular property dependent on the liquid crystalline matrix, can give information on the chiral dopant; furthermore the passage from molecular to macrostructural chirality somehow amplifies the molecular asymmetry, and this can be used to detect traces of optically active substances,[9] to follow racemization kinetics on extremely small-scale experiments[10a,b] and also to characterize molecules with very low optical rotations such as compounds chiral by isotopic substitution.[11]

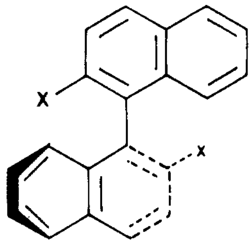
In a previous work on chiral bridged biaryls[12] and related molecules, we found a general correlation between the helicity of the biaryl system and the handedness of the induced cholesteric mesophases: *P*-helicity is correlated to *P*-cholesterics and *M*-helicity to *M*-cholesterics. We also proposed a model of induction in which the chirality is transferred from the chiral inducer to the nearest neighbor molecule of the solvent which adopts the same chiral conformation of the inducer; this solvent molecule serves as a template for the near neighbor and so on, thus justifying the observed high values of β_M.



In this paper we report results concerning the chiral open-chain binaphthyl system.

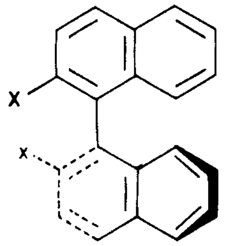
Results and Discussion

Chiral open-chain binaphthyls are not conformationally rigid molecules and, for a given configuration, they can exist in cisoid and transoid conformations displaying opposite helicity of the two naphthalene groups.



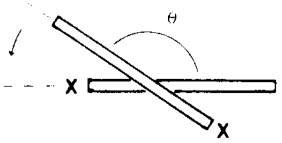
(S) - transoid

θ >90°

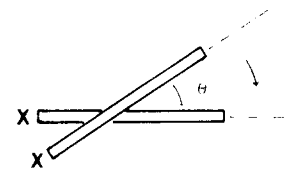


(S) - cisoid

θ< 90°



M - helicity



P - helicity

X-ray diffraction studies indicate that in the crystalline state the actual conformation does not seem to be dependent on only intramolecular interactions but also on crystal packing effects. For example, in racemic crystals, 1,1′-binaphthyl adopts a cisoid conformation (θ = 68°), while in optically active crystals the transoid conformation is present (θ = 103°).[13a,b] Other 4,4′-disubstituted 1,1′-binaphthyls show similar behavior with dihedral angles smaller in the racemic (θ = 68°) and larger in the optically active crystals (θ = 80–102°)[14]. X-ray crystallographic studies for other 1,1′-binaphthyl derivatives report dihedral angles in the range 68–92°.[15]

Information about the conformation of binaphthyls in solution is derived from the analysis of the exciton CD couplet corresponding to the ^1B_b electronic transition of

---

(3) Stegemeyer, H.; Mainush, K. J. *Naturwissenschaften* **1971**, *58*, 599–602.

(4) Gottarelli, G.; Mariani, P.; Spada, G. P.; Samorî, B.; Forni, A.; Solladié, G.; Hibert, M. *Tetrahedron* **1983**, *39*, 1337–1344.

(5) Korte, E. H.; Schrader, B.; Bualeck, S. *J. Chem. Res. Synop.* **1978**, 236–237; *J. Chem. Res. Miniprint* **1978**, 3001–3022.

(6) Ruxer, J. M.; Solladié, G.; Candau, S. *Mol. Cryst. Liq. Cryst.* **1978**, *41*, 109–114.

(7) Gottarelli, G.; Samorî, B.; Stremmenos, C.; Torre, G. *Tetrahedron* **1981**, *37*, 395–399.

(8) Gottarelli, G.; Spada, G. P. *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 377–388.

(9) (a) Penot, J. P.; Jacques, J.; Billard, J. *Tetrahedron Lett.* **1968**, 4013–4016. (b) Korte, E. H. *Appl. Spectrosc.* **1978**, *32*, 568–572; (c) Bertocchi, G.; Gottarelli, G.; Prati, P. *Talanta* **1984**, *31*, 138–140.

(10) (a) Ruxer, J. M.; Solladié, G.; Candau, S. *J. Chem. Res. Synop.* **1978**, *82*–83. (b) Solladié, G.; Zimmermann, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 348–362.

(11) Gottarelli, G.; Samorî, B.; Fuganti, C.; Grasselli, P. *J. Am. Chem. Soc.* **1981**, *103*, 471–472.

(12) Gottarelli, G.; Hibert, M.; Samorî, B.; Solladié, G.; Spada, G. P.; Zimmermann, R. *J. Am. Chem. Soc.* **1983**, *105*, 7318–7321.

(13) (a) Kuroda, R.; Mason, S. F. *J. Chem. Soc., Perkin Trans. 2* **1981**, 167–170. (b) Kress, R. B.; Duesler, E. N.; Etter, M. C.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1980**, *102*, 7709.

(14) Pauptit, R. A.; Trotter, J. *Can. J. Chem.* **1983**, *61*, 69–71.

(15) Harata, K.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2747–2751.

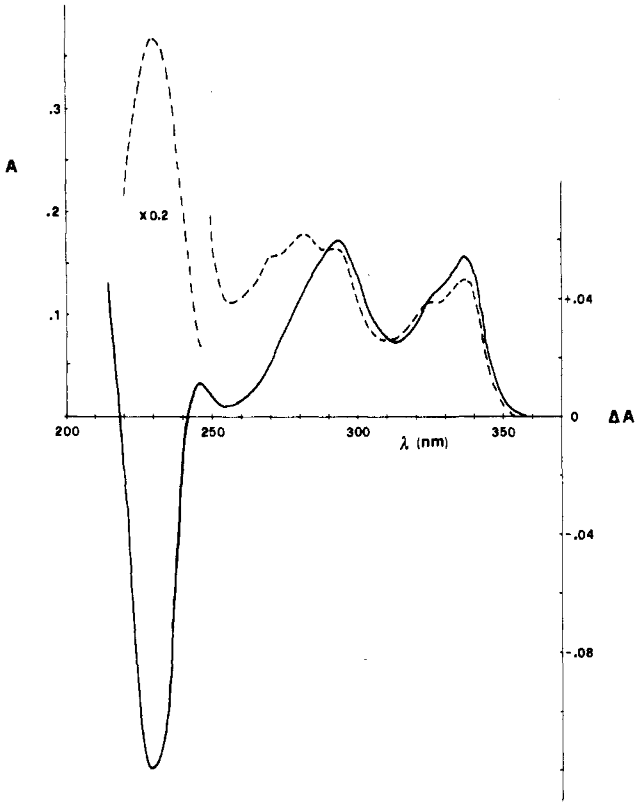


Figure 1. Linear dichroism ($A_{\parallel} - A_{\perp}$, —) and average absorption (($A_{\parallel} + A_{\perp}$)/2, ---) spectra of racemic derivative **5** oriented in the nematic phase ZLI 1167 (a mixture of bicyclohexyl derivatives) recorded at T = 315 K.

the naphthalene chromophore.[16,17] Unsubstituted binaphthyl and 2,2′-disubstituted derivatives (X = CH_3, CH_2OH, COOH, COO^-, $COOCH_3$, NH_2, NH_3^+) all adopt preferred conformations in which the dihedral angle is less than the critical angle at which the bisignate CD intensity vanishes, which is calculated to be 110° in the exciton or 100° in the π-SCF approximations.[16a]

Measurements of the twisting power of open-chain binaphthyls of known absolute configuration should give direct information on the helicity of the biaryl system and hence on the preferred cisoid or transoid molecular conformation. The data obtained for 10 2,2′-disubstituted 1,1′-binaphthyls are reported in Table I.

For compounds **1**–**8** the S absolute configuration is associated with positive values of twisting power β_M. Molecules **9** and **10** instead give β_M of the opposite sign. Quantitative values are considerably smaller than those observed for the rigid binaphthyls (β_M = 55–80 μm^{-1}),[12] the values ranging from 0.5 to ca. 30 μm^{-1}.

In order to verify that the allignment of the open-chain binaphthyls is similar to that of bridged derivatives, i.e., with the twofold symmetry axis perpendicular to the nematic director,[12] we have measured the linear dichroism spectrum of racemic 2,2′-dimethoxy-1,1′-binaphthyl in the nematic phase ZLI 1167 (mixture of bicyclohexyl derivatives). The spectrum (Figure 1) is very similar to that of the bridged homologue reported in ref 12 and can be discussed in a similar way; also in this case the orientation of the solute is with the twofold symmetry axis perpendicular to the nematic director.

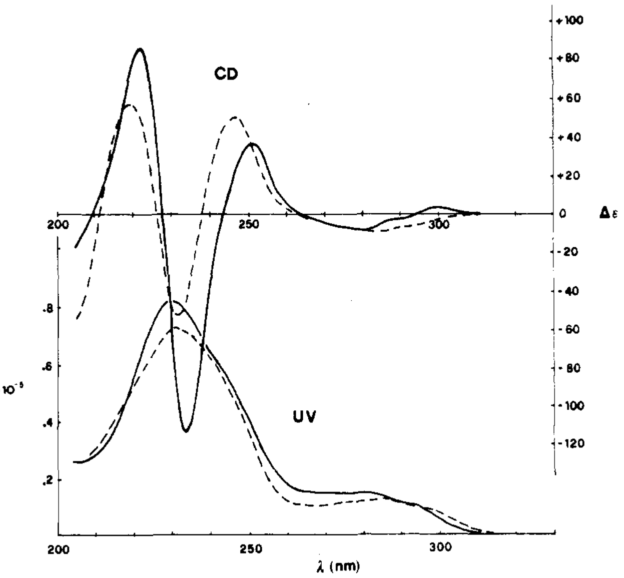


Figure 2. Circular dichroism (upper part) and absorption (lower part) spectra of derivatives **9** (---) and **10** (—) in ethanol.

Therefore the mechanism of cholesteric induction should be similar to that discussed for bridged derivatives: for S configuration, cisoid conformations have P-helicity of the binaphthyl system and should give right-handed cholesterics; transoid conformations have M-helicity and should give left-handed cholesterics.

Our data indicate therefore that derivatives **1**–**8** are in a preferred cisoid conformation, while derivatives **9** and **10** adopt a transoid structure. Derivatives **1**–**3**, whose cisoid conformation is stabilized by hydrogen bonds, show higher values of β_M. The low values of β_M could be associated either to preferred conformations having a dihedral angle of ca. 90° (in similar cases very low values of β_M were observed[8]) or to the existence of nearly equally populated cisoid and transoid conformations.

Some uncertainties are still present for derivatives **7** and **8** displaying very small values of β_M due to the fact that intrinsic value of the twisting power for rigid transoid derivatives are not available and might not be equal and opposite. However, preliminary results from rigid cisoid and transoid diaminobiphenyl derivatives indicate values of equal magnitude and opposite sign.[18]

Our conclusions are in excellent agreement with those obtained from CD spectroscopy for derivatives **2**, **4**, and **8**.[16,17]

We have recorded the CD spectra of derivatives **9** and **10** (Figure 2), and indeed a dramatic sign inversion of the couplet centered at ca. 230 nm (^1B_b transition of the naphthalene chromophore) with respect to cis-bridged binaphthyls[16] and derivatives **2**, **4**, and **8** is observed. This indicates that the bulky CH_2Br and $CHBr_2$ groups force the system to transoid conformations.

On the other hand, X-ray diffraction work on derivative **9** also indicates a transoid conformation.[15]

Conclusion

The helicity of optically active biaryl molecules is likely to be the main factor determining their twisting power in nematic liquid crystals.

As in the case of bridged biaryl compounds, the chirality of the dopant is transferred to the nematic through chiral

---

(16) (a) Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* **1974**, *30*, 1671–1682. (b) Kuroda, R.; Mason, S. F. *Tetrahedron* **1981**, *37*, 1995–1999.

(17) Harada, N.; Nakanishi, K. "Circular Dichroic Spectroscopy-Exciton Coupling in Organic Stereochemistry"; Oxford University Press: Oxford, 1983.

(18) Gottarelli, G.; Spada, G. P.; Seno, K.; Hagishita, S.; Kuriyama, K. *Bull. Chem. Soc. Jpn.*, in press.

J. Org. Chem. 1986, 51, 592–596

conformations. However, open-chain binaphthyls can exist for a given absolute configuration in cisoid and transoid conformations of opposite helicity. Our results demonstrate that the sign of β_M is determined by the dihedral angle between the two aromatic parts. Therefore it is possible to determine the conformation of biaryls from the sign of their twisting power: cisoid conformations giving right-handed cholesterics and transoid conformations left-handed cholesterics for the *S* absolute configuration.

Experimental Section

Pitch values were measured at room temperature by means of the "droplet method"[19] using a Leitz Ortholux microscope and/or with the "lens" version of the Grandjean–Cano method[20] using a Zeiss Standard 16 microscope.

Helical handedness was determined from the sign of the rotatory power[21] and from the sense of the spiral-like disclination observed under circular boundary conditions.[22]

The linear dichroism and average absorption spectra were recorded by a modulated technique with a JASCO J-500A spectropolarimeter equipped with LD attachment. The liquid crystalline matrix was obtained by using a bicyclohexyl nematic, transparent to the UV radiation (ZLI 1167 from Merck) and a surface coupling agent in order to get linearly anisotropic samples (the experimental details are discussed in ref 23).

The CD spectra were recorded at room temperature with a JASCO J-500A spectropolarimeter equipped with a DP-500 data processor. Absorption spectra were recorded with a JASCO UVIDEC-510 spectrophotometer and/or a Varian DMS 90 spectrophotometer.

Compounds **4**[16a] and **8**[24] were kindly supplied by Professor S. F. Mason. Compound **1** was a commercial product. Compounds **7**, **9**, and **10** were kindly supplied by Dr. J. P. Mazaleyrat.[25] Molecules **3**, **5**, and **6** were kindly supplied by Dr. M. Hibert and **2** by Dr. Welwart.

Acknowledgment. We are indebted to NATO for the partial support of this research (Grant GR 081-81). G.G. and G.P.S. thank CNR and MPI (Rome) for financial support. G.S., R.B., and R.Z. thank CNRS (UA 466) for financial support.

We are grateful to Professor S. F. Mason for derivatives **4** and **8**, Dr. J. P. Mazaleyrat for compounds **7**, **9**, and **10**, Dr. M. Hibert for compounds **3**, **5**, and **6**, and Dr. Welwart for molecule **2**.

Registry No. **1**, 18531-99-2; **2**, 76373-23-4; **3**, 51751-91-8; **4**, 18531-95-8; **5**, 75640-87-8; **6**, 99747-67-8; **7**, 99764-91-7; **8**, 32587-64-7; **9**, 37803-02-4; **10**, 98834-91-4; K15, 40817-08-1; E7, 63748-28-7.

---

[19] Seuron, P.; Solladié, G. *Mol. Cryst. Liq. Cryst.* **1979**, *56*, 1–6.

[20] Heppke, G.; Oestreicher, F. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1977**, *A32*, 899–901.

[21] Berthault, J. P. Thèse, Universite' de Paris, 1977.

[22] Heppke, G.; Oestreicher, F. *Mol. Cryst. Liq. Cryst. Lett.* **1978**, *41*, 245–249.

[23] Samorì, B.; Mariani, P.; Spada, G. P., *J. Chem. Soc., Perkin Trans. 2* **1982**, 447–453.

[24] Harris, H. E.; Harris, M. M.; Mazengo, R. Z.; Singh, S. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1059–1063.

[25] Maigrot, N.; Mazaleyrat, J. P. *Synthesis* **1985**, 317–320.

Transannular Interactions in Difunctional Medium Rings. 1. n/π Interactions in Cyclic Amino Ketones and Aminoalkenes Studied by Photoelectron Spectroscopy

Gerhard Spanka and Paul Rademacher*

Institute of Organic Chemistry, University of Essen, D-4300 Essen, West Germany

Received October 4, 1985

The He I photoelectron spectra of the cyclic and bicyclic amino ketones **1**–**4** and aminoalkenes **5**–**8** have been recorded and interpreted with respect to transannular interactions of the functional groups. The interactions have been determined by comparing the spectra of **1**–**8** with those of the monofunctional compounds **9**–**20**. For **1**–**4** the n_O ionization can be considered as an indicator of transannular interaction. For **5**–**8** the amount of interaction is measured by the shifts of the n_N and the π_{CC} orbitals. The results indicate considerable n/π interactions in the eight-membered rings of **2** and **6**. Of the compounds with a ten-membered ring, there is only interaction in amino ketone **3**, while it is virtually absent in aminoalkene **7**. Conformations are proposed to account for these findings.

Transannular interactions[1-3] are of prominent importance for the structure and the reacivity of medium-sized cyclic compounds. The existence of certain conformations, in which opposite sides of the ring come into close proximity to each other, is a unique feature of medium-ring structure.[1] Transannular reactions are frequently observed for ionic, free radical, and carbenoid attack on unsaturated medium rings, and also transannular cycloaddition is observed in appropriate systems.[2] The chemistry of compounds with two functional groups may be dominated by transannular interactions between the functionalities.[2] Due to the restricted flexibility of a cyclic molecule, the relative positions of the interacting groups can be estimated to a higher degree than in analogous acyclic molecules or in systems composed of monofunctional molecules. As has been expressed by the structure-correlation method of Dunitz and Bürgi,[4] intramolecular interactions can serve as models for intermolecular interactions.

---

[1] Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962. Eliel, E. L. "Stereochemie der Kohlenstoffverbindungen"; Verlag Chemie: Weinheim, 1966. Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Interscience: New York, 1965. Dunitz, J. D. "X-Ray Analysis and the Structure of Organic Molecules";: Cornell University Press: Ithaca, 1979.

[2] Reviews of transannular reactions: Cope, A. C.; Martin, M. M.; McKervey, M. A. *Q. Rev., Chem. Soc.* **1966**, *20*, 119. Ferguson, L. N. "Highlights of Alicyclic Chemistry", Franklin: Palisade, New Jersey, 1973, Part 1, pp 150–180. Haufe, G.; Mühlstädt, M. *Z. Chem.* **1979**, *19*, 170.

[3] Leonard, N. J. *Acc. Chem. Res.* **1979**, *12*, 423.

[4] Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.