Application of NMR Spectroscopy of Chiral Association Complexes

13[†]—Electron Donor-Acceptor Complexes between Racemic Carbazolo[3,4-c]carbazoles and an Optically Active Acceptor

Siddik İçli,*‡ Thomas Burgemeister and Albrecht Mannschreck Institut für Organische Chemie, Universität Regensburg, D-8400 Regensburg, FRG

Maximilian Zander

Rütgerswerke AG, Kekuléstrasse 30, D-4620 Castrop-Rauxel, FRG

Strong electron donor-acceptor (EDA) association between carbazolo[3,4-c]carbazoles and an optically active tetranitrofluorenone derivative was detected by UV-visible spectroscopy and by ¹H NMR shifts. ¹H NMR splittings at low temperatures are due to diastereomeric association complexes and, thus, prove the chirality of carbazolocarbazoles.

INTRODUCTION

Identification of diastereomeric electron donor-¹H NMR (EDA) acceptor complexes by spectroscopy¹⁻³ may be used to measure enantiomeric purity and to suggest the relative orientation of the components in the complex. Recently, this method has applied³ been to chiral phenanthrenes and benzo[c]phenanthrenes and a tetranitrofluorenone derivative (R)-1. The observation of significant chemical shift differences between signals for the enantiomeric donor molecules in the association complex suggested a high π -donor capacity for these condensed aromatic ring systems. Thus, we have selected 5,10dihydrocarbazolo[3,4-c] carbazole⁴ (2) and its derivatives 3 and 4; the helical chirality of these aromatic



* Author to whom correspondence should be addressed at Ankara. † For Parts 12, 11 and 10 of the above series, see Refs 16, 17 and 18, respectively.

[‡] On leave of absence from the Department of Chemistry, Middle East Technical University, Ankara, Turkey.

compounds should give rise to (M) and (P) enantiomers, which are expected to have a higher ability to form π -donor complexes than the previously studied donors.

EXPERIMENTAL

Preparations

(±)-(**RS**)-2-(2,4,5,7-Tetranitrofluoren-9-ylideneaminooxy)propionic acid methyl ester (1)^{5a}. (±)-Isopropylideneaminooxypropionic acid was subjected to reaction with 2,4,5,7-tetranitrofluorenone and a catalytic amount of sulphuric acid. The acid was treated with methanolsulphuric acid to form (±)-1 in 94% yield, m.p. 165-166 °C (lit.^{5a} m.p., 161-164.5 °C).

(-)-(R)-2-(2,4,5,7-Tetranitrofluoren-9-ylideneaminooxy)propionic acid methyl ester (1)^b. This was synthesized by the same method as for the previous compound. Esterification of the acid yielded 67% (-)-1, m.p. 194.0-194.5 °C, $[\alpha]_D^{26} = -77.1 \circ ml g^{-1} dm^{-1}$, c =2.88 mg ml⁻¹ in dioxane (lit.⁶ m.p., 191.0-191.7 °C, $[\alpha]_D^{26} = -78.7 \circ ml g^{-1} dm^{-1}$, c = 0.791 in dioxane). The enantiomeric purity of (-)-1 was calculated to be $94 \pm 10\%$ from $[\alpha]_D^{22} = -97.7 \circ ml g^{-1} dm^{-1}$, $c = 2.99 \text{ mg ml}^{-1}$ in CHCl₃, and $[\alpha]_D^{22} =$ $-104 \circ ml g^{-1} dm^{-1}$, $c = 2.94 \text{ mg ml}^{-1}$ in CHCl₃ for pure (-)-1.³ The δ values at 25 °C are given in Tables 1 and 2.

(MP)-5,10-Dihydrocarbazolo[3,4-c]carbazole (2). This was synthesized as described previously.⁴

(MP)-5,10-Dimethylcarbazolo[3,4-c]carbazole (3). To 380 mg (1.2 mmol) of 2, dissolved in the minimum amount of dry tetrahydrofuran (THF), were added 630 mg (5.0 mmol) of dimethyl sulphate and 1 ml of 50% NaOH solution in water. The mixture was refluxed

CCC-0030-4921/82/0020-0145\$03.00

Table 1.	The chemical shifts, δ , for the protons of 1 and 2, the average chemical shifts, δ	b, and the differences of the
	average chemical shifts, $\Delta \overline{\delta} = \overline{\delta}(-70 \text{ °C}) - \overline{\delta}(25 \text{ °C})$, for the protons of a mixtur	e of 1 and 2 $(1:2=0.74)$ in
	acetone- d_6 upon change of temperature (cf. Fig. 3) (ppm) [*]	

	1						2						
	H-1	H-3	H-6	H-8	CMe	CHMe	OCH₃	H-1	H-2	H-3	H-4	H-6	H-7
δ(25 °C) ^ь	9.62	9.00	8.95	8.90	1.88	5.42	3.84	7.87	7.15	7.41	7.70	7.73	8.01
δ̄(25 ℃)	9.18	8.71	8.62	8.41	1.68	5.08	3.83	7.75	7.07	7.34	7.61	7.58	7.82
δ(−70 °C)	8.31	8.07	7.95	7.35	1.43	4.37	3.86	7.32	6.86	7.20	7.44	7.21	7.40
$\Delta \bar{\delta}$	-0.87	-0.64	-0.67	-1.06	-0.25	-0.71	0.03	-0.43	-0.21	-0.14	-0.17	-0.37	-0.42
^a A negativ ^b P. Roza, F	e sign me Ph.D. The	eans shif sis, Univ	ts to hig ersität R	iher field Iegensbu	l upon lo Irg, FRG,	wering 1979.	the ter	nperatur	e.				

(water-bath) for 2–3 h, THF was partially distilled off and water was added. Crude **3** was obtained in quantitative yield by filtration. Two recrystallizations from ethyl acetate–THF (1:1) gave 310 mg (75%) of **3**, m.p. 277–278 °C. For $C_{24}H_{18}N_2$ (mol. wt. 334.4): calculated C 86.20, H 5.42, N 8.38; found C 86.27, H 5.35, N 8.37%.

(MP)-5,10-Dibenzylcarbazolo[3,4-c]carbazolo (4). To 400 mg (1.3 mmol) of 2, dissolved in the minimum amount of dry THF, were added 70 mg (2.4 mmol) of sodium hydride/20% paraffin oil. The suspension was stirred at room temperature for 1 h, followed by heating (water-bath) at 40 °C for 0.5 h. A solution of 690 mg (4.0 mmol) of benzyl bromide in 5 ml of THF was added dropwise, and reflux at 40 °C was continued for 1 h. Water (25 ml) was added and the organic layer was extracted with ethyl acetate, dried and the solvent removed to yield crude 4. Three recrystallizations from benzene gave 380 mg (66%) of analytically pure 4, m.p. 255 °C. For $C_{36}H_{26}N_2$ (mol. wt. 486.6): calculated C 88.86, H 5.39, N 5.76; found C 88.86, H 5.49, N 5.43%.

UV and NMR spectra

The UV spectra of 1 were recorded in acetone on a Beckman Acta MVI spectrophotometer operating with automatic deuterium and tungsten lamps. Low-temperature spectra were measured in combination with a Beckman Model CTC 250 temperature controller, with an accuracy of ± 1 °C.

The ¹H NMR spectra were recorded in the pulse FT mode at 90 MHz on a Bruker WH-90 spectrometer with an 8K data point capacity for FID. For the structure determinations and signal assignments the measuring conditions were as follows: sweep

18 Hz cm⁻¹, pulse width 2.1 μ s, number of scans 40– 70. The chemical shifts and frequencies were ± 0.01 ppm and ± 0.5 Hz, respectively. The temperature control was performed with a Bruker BST 100/700 unit. Tetramethylsilane (TMS) was used as internal standard and typical ¹H NMR solutions were 5–40 mM. The solvents and the standards were products of E. Merck, Darmstadt, FRG.

Computer simulations

The simulation of the aromatic proton signals was carried out on a TR 440 computer (Computer Gesellschaft, Konstanz, FRG) using the LAME^{7a} (LAOCOON^{7b} with magnetic equivalence) program. These calculations require coupling constants, the number of non-equivalent nuclei and the estimated chemical shifts as input to obtain the best fit between experimental and simulated spectra.

RESULTS AND DISCUSSION

A charge-transfer interaction between 1 and 2 was observed in the UV-visible spectra (Fig. 1), which exhibited an additional EDA band at 608 nm. This band intensified appreciably at lower temperatures, consistent with the presence of higher concentrations of the EDA complex. A second overlapping EDA band is present near 450 nm (Fig. 1).

The ¹H NMR spectra of the aromatic protons of carbazolocarbazoles are complex; a correct analysis of the chemical shifts (Table 3 and Fig. 2) was necessary, however, for these studies. Literature data of related compounds were not sufficient for an unambiguous assignment of H-6 and H-7. Thus, ¹H{¹H} NOE-difference spectroscopy was applied to **3** in CDCl₃ at

Table 2. The chemical shifts, δ , for the protons of 1 and 3, the average chemical shifts, $\overline{\delta}$, and the differences of the average chemical shifts, $\Delta \overline{\delta} = \overline{\delta}(-70 \ ^{\circ}\text{C}) - \overline{\delta}(25 \ ^{\circ}\text{C})$, for the protons of a mixture of 1 and 3 (1:3=0.90) in acetone- d_6 upon change of temperature (cf. Fig. 4) (ppm) "

	<u> </u>						3					
	H-1	H-3	H-6	H-8	CMe	CHMe	OCH3	H-2	H-3	H-6	H-7	Me
δ(25 °C) ^ь	9.62	9.00	8.95	8.90	1.88	5.42	3.84	7.17	7.49	7.81	8.11	4.15
δ̄(25 ℃)	9.39	8.83	8.74	8.63	1.75	5.22	3.84	7.11	7.44	7.70	7.99	4.09
δ̄(−70 °C)	8.66	8.21	8.05	7.54	1.52	4.46	3.87	7.03	7.24	7.37	7.66	3.88
$\Delta ar{\delta}$	-0.73	-0.62	-0.69	-1.09	-0.23	-0.76	0.03	-0.08	-0.20	-0.33	-0.33	-0.21

^a A negative sign means shifts to higher field upon lowering the temperature. ^b P. Roza, Ph.D. Thesis, Universität Regensburg, Regensburg, FRG, 1979.



Figure 1. UV spectra of (RS)-1 (2.20×10^{-3} M), (MP)-2 (2.16×10^{-3} M) and a mixture of (RS)-1 (2.2×10^{-3} M) and (MP)-2 (2.2×10^{-3} M) in acetone at 20 °C.



Figure 2. Experimental (above) and simulated (below) ¹H NMR spectra for (*MP*)-5,10-dihydrocarbazolo[3,4-c]carbazole (2). The experimental spectrum was recorded at a concentration of 0.03 m in acetone- d_6 at 25 °C. The simulated spectrum is only plotted for the 1-, 2-, 3- and 4-protons. The parameters are given in Table 3.

Tat)le 3.	Param carbaz 25 °C	eters colocai	used to bazolo	es 2 (cf. Fi	lation g. 2),	, 3 and	4 in	MK spectra acetone-d ₆	ot at
	δ1	δ₂	δ3	δ4	δ_6	δ7	δ _{CH3}	δ _{CH2} (ppm))		
2	7.87	7.15	7.41	7.70	7.73	8.01	—				
3	7.85	7.17	7.49	7.73	7.81	8.11	4.15				

7.95

J(24)

J(25)

5.84

J(34)

J(35)

J(45) J(67) (Hz)

6.9 7.9 1.3 0.8 0.6 1.3 7.9 0.0 8.7 2 0.0 0.0 3 8.2 1.3 0.8 7.0 1.3 8.2 9.0 ----4 8.0 1.2 0.8 7.0 1.2 8.0 8.8 * The coupling constants were directly measured from the experimental spectra; no changes were found to be necessary. The chemical shifts were initially estimated, then varied until the best fit was found.

room temperature. A NOE effect was observed for the upfield half of the AB system of H-6 and H-7 when the methyl protons were irradiated. The low-field half remained unaffected and it is, therefore, assigned to H-7. The remaining protons form an ABCDE system in $\mathbf{2}$ and an ABCD system in $\mathbf{3}$ and $\mathbf{4}$, for which computer simulations of the experimental spectra (e.g. Fig. 2) were carried out. The parameters of these derivatives are found not to vary significantly (Table 3).

7.91

J(12)

7.12

J(13)

7.37

J(14)

7.61

J(15)

7.68

J(23)

4

Upfield shifts were observed for all the proton signals (except OCH₃) at 25 °C on going from the free molecules to the mixtures 1-2 and 1-3 (Tables 1 and 2; Figs 3 and 4). A similar trend of upfield shifts (Tables 1 and 2; Figs 3 and 4) was also observed for all the proton signals (except OCH₃) in the mixtures of 1-2 and 1-3 on lowering the temperature from 25 to -70 °C. These findings are in agreement with the UV-visible spectral observations that the relative concentrations of the EDA complexes increase at lower temperatures. The upfield shifts mentioned are the differences of the average chemical shifts, $\Delta \overline{\delta}$; the difficulties of the experimental work and the conditions did not allow the measurement of the limiting shifts. The $\Delta \overline{\delta}$ values for the aromatic protons of **1** were found to be two to three times larger than for other complexes of 1 studied earlier.^{2,3} This is be-



Figure 3. Differences of average chemical shifts, $\Delta \overline{\delta}$, for the protons of a mixture of 1 and 2 ([1]:[2]=0.74) in acetone- d_6 on change of temperature. A negative sign means shifts to higher field on lowering the temperature.

lieved to result from the greater π -electron donor capacity of carbazolocarbazoles.

It is apparent from Figs 3 and 4 that the aromatic proton signals of the acceptor are shifted further upfield than those of the donor on lowering the temperature. The transfer of π -electron density from the donor to the acceptor is expected⁸ to cause an upfield shift of the signals of the acceptor. If this charge transfer were the only effect, the signals of the donor should be shifted downfield on complex formation or on lowering the temperature of the mixtures.⁹ The observed upfield shifts of the signals of the donor, although smaller than those of the acceptor, are explained by a competing magnetic anisotropy influence,⁸ which causes upfield shifts of all aromatic signals in $\pi - \pi$ complexes. The signals of H-1 and H-8 of the tetranitrofluorenone derivative 1 are shifted further upfield than those of H-3 and H-6 on lowering the temperature and, also, $|\Delta \bar{\delta}(H-8)| > |\Delta \bar{\delta}(H-1)|$ (Tables 1 and 2; Figs 3 and 4). This may indicate that the acceptor 1 approaches the donor molecule-in the average structure of the complexfrom the aliphatic chain side of its aromatic ring (H-1 and H-8 side), and more towards the H-8 side because of less steric hindrance.

The chirality of 2 has been suggested earlier, but no experimental evidence was given.⁴ We have proven



Figure 4. Differences of average chemical shifts, $\Delta \overline{\delta}$, for the protons of a mixture of 1 and 3 ([1]:[3] = 0.90) in acetone- d_6 on change of temperature. A negative sign means shifts to higher field on lowering the temperature.



Figure 5. ¹H NMR of *N*-CH₃ for (*MP*)-3 and of *O*-CH₃ for (*R*)-1 for an equimolar mixture in acetone- d_6 at ~50 °C. The *N*-CH₃ signal of (*MP*)-3 is split because of diastereomeric association complexes.

the chirality of 2 and 3 from their diastereometric EDA complexes (shown for 2) with (R)-1.

$$(M)-2+(P)-2+2(R)-1 = [(M)-2\cdots(R)-1]+[(P)-2\cdots(R)-1]$$

These were detected by low-temperature NMR (e.g. Fig. 5). The measured splittings, $\Delta\Delta\bar{\delta}$, for (*MP*)-2 and (*MP*)-3 are given in Table 4. Splitting differences for H-6 and H-7 are slightly larger than for H-2 and H-3. The shift differences, $\Delta\bar{\delta}$, for H-1, H-6 and H-7 of the donors were also found to be larger than for H-2, H-3 and H-4 (Figs 3 and 4). Molecular orientations in 1:1 diastereomeric EDA complexes between hexahelicenes and the acid derived from 1 have been suggested previously.¹⁰ It is difficult to explain all the upfield shifts in Figs 3 and 4 and the diastereomeric splittings of the donors 2 and 3 on the basis of a single orientation. The acceptor molecules; a second equilibrium may, thus, be involved, as shown for 2:

$$2+1 \rightleftharpoons [2 \cdots 1]$$
$$1+[2 \cdots 1] \rightleftharpoons [1 \cdots 2 \cdots 1]$$

Thermodynamic parameters for the EDA association of a hexahelicene with **1** have been reported;¹¹ the authors did not indicate, however, if a second equilibrium could be excluded by their data.

A lower limit of 57 kJ mol⁻¹ for the free enthalpy of racemization, ΔG^{\neq} , of **2** has been calculated from the highest temperature (-30 °C) at which a splitting of $\Delta \Delta \delta = 0.03$ ppm at 90 MHz was still visible. Pentahelicene has a free enthalpy of racemization, ${}^{12}\Delta G^{\neq}$, of

Table 4.	Differences, $\Delta\Delta\bar{\delta}$, of the average ¹ H chemical shifts
	for the protons of the (M) and (P) enantiomers of
	2 and 3 in the presence of (R)-1 in acetone- d_6^*

	$\Delta\Delta \vec{\delta}_2$	$\Delta\Delta\delta{ar\delta}_3$	$\Delta \Delta \tilde{\delta_5}^{b}$	$\Delta\Delta\delta_6$	$\Delta\Deltaar{\delta_7}$
2	0.01	0.01	0.02	0.03	0.02
3	0.01	0.01	0.03	0.03	0.04

* [1]: [2] = 0.61 at -61.5 °C and [1]: [3] = 0.90 at -70 °C. In the case of H-1 and H-4 only broadened lines are observed due to the overlapping of many signals. ^b $\Delta\Delta\delta_{s}$ is for N-H in 2 and N-CH₃ in 3.

101.2 kJ mol⁻¹ between 31 and 47 °C. A ΔG^{\neq} value of 92.4 kJ mol⁻¹ between 10 and 25 °C was determined for a heterohelicene^{13a} with three benzene and three thiophene rings. The carbazolocarbazoles studied here are expected to have a similar ΔG^{\neq} value, since they are of similar size. (The molecular sizes of **2** and the above-mentioned heterohelicene were compared in models built with estimated^{13b} bond lengths and bond angles.)

The 5,10-dibenzyl derivative 4 was prepared with the expectation that the diastereotopic methylene protons would exhibit an AB spectrum. Despite numerous attempts, only a single broadened line was observed in several media at temperatures between 25 and -50 °C.

The aromatic proton signals of 1 in some mixtures, mostly mixtures of 1 and 3, were seen to be broadened on mixing at 25 °C. After several hours this broadening disappeared, and the expected resolved signals were observed. Apparently, a π -electron transfer from donor to acceptor forms a donor cation and an acceptor anion radical. These radical ions have been detected by ESR^{14,15} in some solutions of strong donors, D, and acceptors, A.

$$D+A \rightleftharpoons [D]^{++} + [A]^{-+}$$

Our ESR study of a solution of 1 and 3 in acetone d_6 showed a weak and a broad ESR signal at room temperature, which weakened and disappeared after several hours. More detailed ESR studies with better resolution are now being carried out, and these may identify the structures of the species present.

Acknowledgements

The authors thank Mr J. Zieger, Regensburg, for performing the syntheses, and Mr. H. Scherübl, Regensburg, for discussions. Research support from the Alexander von Humboldt Foundation of the Federal Republic of Germany is appreciated. Dr L. Ernst, Braunschweig-Stöckheim, kindly provided the ¹H{¹H} NOE difference spectra. The authors are also indebted to Professor J. Hüttermann, Regensburg, for providing the ESR spectra.

REFERENCES

- W. H. Pirkle and D. L. Sikkenga, J. Org. Chem. 42, 1370 (1977).
- A. Mannschreck, P. Roza, H. Brockmann, Jr., and T. Kemmer, Angew. Chem. 90, 955 (1978); Angew. Chem. Int. Ed. Engl. 17, 940 (1978).
- T. Burgemeister, P. Roza, H. Scherübl and A. Mannschreck, unpublished results.
- 4. M. Zander and W. H. Franke, Chem. Ber. 102, 2728 (1969).
- (a) M. S. Newman and W. B. Lutz, J. Am. Chem. Soc. 78, 2469 (1956); (b) P. Block, Jr, and M. S. Newman, Org. Synth. 48, 120 (1968).
- G. Briegleb, K. Henschel and H. G. Kuball, Z. Phys. Chem., N.F. 46, 229 (1965).
- 7. (a) C. W. Haigh, in Annual Reports on NMR Spectroscopy,

edited by E. F. Mooney, Vol. 4, p. 311, Academic Press, New York, (1971); (b) A. A. Bothner-By and S. Castellano, J. Chem. Phys. 41, 3863 (1964).

- 8. R. Foster, Organic Charge-Transfer Complexes, p. 113, Academic Press, London (1969).
- 9. J. Yarwood, Chem. Commun. 809 (1967).
- 10. J. M. Brown, I. P. Field and P. J. Sidebottom, Tetrahedron Lett. 4867 (1981).
- A. Balan and E. H. Gottlieb, J. Chem. Soc., Perkin Trans. 2, 350 (1981).
- 12. C. Goedicke and H. Stegemeyer, Tetrahedron Lett. 937 (1970).
- (a) H. Wynberg, Acc. Chem. Res. 4, 65 (1971); (b) H. Wynberg and M. B. Groen, Chem. Commun. 964 (1969).

- 14. E. M. Kosower, Prog. Phys. Org. Chem. 3, 81 (1965).
- 15. H. H. Kolodny and K. W. Bowers, J. Am. Chem. Soc. 94, 1113 (1972).
- R. Küspert and A. Mannschreck, Org. Magn. Reson. 19, 6 (1982).
- 17. M. Holík, M. Turečková, A. Mannschreck and G. Stühler, Org. Magn. Reson. 19, 121 (1982).
- 18. W. Offermann and A. Mannschreck, *Tetrahedron Lett.* 3227 (1981).

Received 4 January 1982; accepted (revised) 19 May 1982