The Structures of Indolyl(alkoxy)carbenium Tetrafluoroborates: A New Class of Highly Stabilized Carbenium Ions

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Z. Naturforsch. **44b,** 659–665 (1989); received February 16, 1989

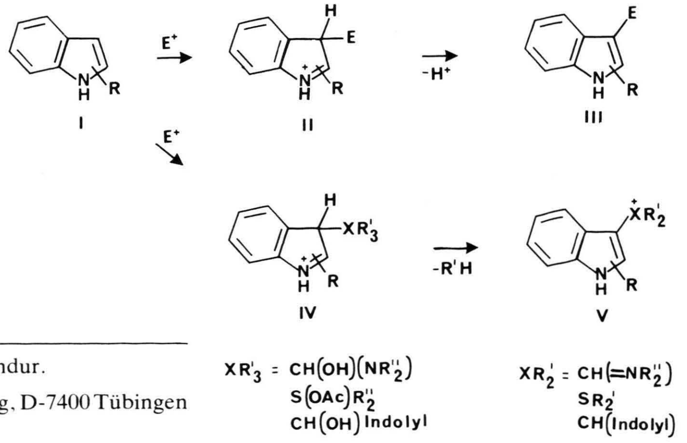
^{1}H NMR Spectra, ^{13}C NMR Spectra, Crystal Structure,
Indolyl(alkoxy)carbenium Tetrafluoroborates

The conformations of and charge distributions in indolyl(alkoxy)carbenium tetrafluoroborates **2,** a new class of highly stabilized carbenium ions, were investigated by ^{1}H and ^{13}C NMR spectroscopy and the crystal structure of indol-3-yl(methoxy)phenylcarbenium tetrafluoroborate (**2e**) was determined by X-ray diffraction methods. The phenyl-substituted cation of **2e** exhibits axial chirality in the crystalline state.

Introduction

The regiospecific electrophilic substitution of 3-unsubstituted indoles **I** functioning as heterocyclic enamines represents one of the most thoroughly investigated fields of indole chemistry with regard to preparative and mechanistic aspects [1–6] (Scheme 1). The regiochemistry (selective 3-substitution) can be predicted by means of, for example, the excellent stabilization of the transition state in the reaction of **I** to form the σ-complex **II** [4]. In the course of electrophilic substitution reactions of 3-unsubstituted indoles **I** with particular electrophiles, the intermediate **II** can, in addition to the formation of **III,** also undergo stabilization through a selective 1,2-elimination to form **V** *via* **IV** in those cases where a leaving group 'R'H' is introduced by way of the electrophile (El in **IV** = XR'$_3$). The excellent stabilization of a cationic center by a 3-indolyl moiety, such as in **V,** has now been clearly established by numerous examples [7–9].

We have already reported the first preparations of a series of previously unknown 3-indolyl(alkoxy)carbenium tetrafluoroborates **2a–2f**′ as thermally stable, crystalline compounds by reactions of *ortho* esters or dialkoxycarbenium tetrafluoroborates with 3-unsubstituted indoles **1a–1d** [10–13] (Scheme 2). Up to date, we have only described the preparative aspects and reactivities of these ambident, highly stabilized carbenium ions. In the present paper, we now report on a ^{1}H and ^{13}C NMR spectroscopic in-



Scheme 1.

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[*] Reprint requests to Prof. Dr. Ulf Pindur.

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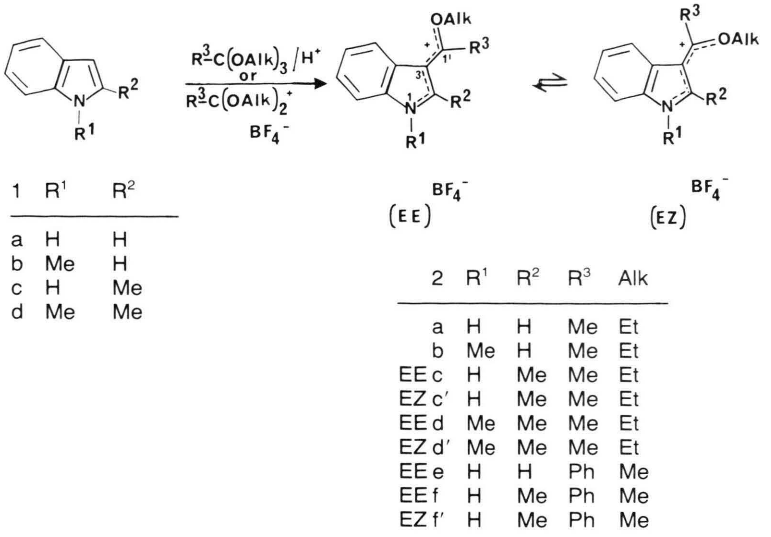


1	R¹	R²
a	H	H
b	Me	H
c	H	Me
d	Me	Me

2	R¹	R²	R³	Alk
a	H	H	Me	Et
b	Me	H	Me	Et
EE c	H	Me	Me	Et
EZ c'	H	Me	Me	Et
EE d	Me	Me	Me	Et
EZ d'	Me	Me	Me	Et
EE e	H	H	Ph	Me
EE f	H	Me	Ph	Me
EZ f'	H	Me	Ph	Me

Scheme 2.

vestigation of the structure (conformation, configuration, charge distribution) of **2.** In one case, and as a representative example of this new class of compounds, we have also been able to carry out an X-ray diffraction study to analyse the conformation (or configuration) of the compounds in the crystal state.

Results and Discussion

^1H and ^{13}C NMR spectroscopic investigations of compounds **2**

The cations of **2** can, in principle, exist as mixtures of <u>EE</u>- and <u>EZ</u>-conformers with an almost coplanar

Table I. ^1H NMR Chemical shift data for compounds **2** at 20 °C [δ scale (ppm)]. Solvent for **2a–2e:** CD_3NO_2, for **2f, 2f':** CD_2Cl_2.

Compound (MHz)	Chemical shifts
2a (400)	1.75 (t, ^3J = 7.0 Hz, 3H, $CH_2-C\underline{H}_3$), 3.06 (s, 3H, C1'–CH_3), 4.97 (q, ^3J = 7.0 Hz, 2H, $C\underline{H}_2-CH_3$), 7.52 (mc, 2H, C5–H, C6–H), 7.75 (mc, 1H, C7–H), 8.13 (mc, 1H, C4–H), 8.92 (d, ^3J = 4.16 Hz, 1H, C2–H), 11.4 (br. s, 1H, NH)
2b (400)	1.74 (t, ^3J = 7.03 Hz, 3H, $CH_2-C\underline{H}_3$), 3.03 (s, 3H, C1'–CH_3), 4.10 (s, 3H, N–CH_3), 4.94 (q, ^3J = 7.04 Hz, 2H, $C\underline{H}_2-CH_3$), 7.60 (mc, 2H, C5–H, C6–H), 7.72 (mc, 1H, 1H, C7–H), 8.15 (mc, 1H, C4–H), 8.90 (s, 1H, C2–H)
2c (400)	1.74 (t, ^3J = 7.03 Hz, 3H, $CH_2-C\underline{H}_3$), 2.96 (s, 3H, C2–CH_3), 2.99 (s, 3H, C1'–CH_3), 4.88 (q, overlapping, 2H, $C\underline{H}_2-CH_3$), 7.47 (mc, overlapping, 2H, C5–H, C6–H), 7.60 (mc, 1H, C7–H), 8.08 (dd, ^3J = 6.3 Hz, ^4J = 2.2 Hz, 1H, C4–H), 11.23 (br. s, 1H, NH)
2c' (400)	1.67 (t, ^3J = 7.03 Hz, 3H, $CH_2-C\underline{H}_3$), 2.87 (s, 3H, C2–CH_3), 3.09 (s, 3H, C1'–CH_3), 4.88 (q, overlapping, 2H, $C\underline{H}_2-CH_3$), 7.47 (mc, overlapping, 2H, C5–H, C6–H), 7.64 (mc, 1H, C7–H), 7.90 (dd, ^3J = 6.7 Hz, ^4J = 2.0 Hz, 1H, C4–H), 11.23 (br. s, 1H, NH)
2d (400)	1.74 (t, ^3J = 7.0 Hz, 3H, $CH_2-C\underline{H}_3$), 2.99 (s, 3H, C2–CH_3), 3.05 (s, 3H, C1'–CH_3), 3.97 (s, 3H, NCH_3), 4.9 (q, overlapping, 2H, $C\underline{H}_2-CH_3$), 7.55 (mc, overlapping, 2H, C5–H, C6–H), 7.66 (mc, 1H, C7–H), 8.17 (mc, 1H, C4–H)
2d' (400)	1.68 (t, ^3J = 7.0 Hz, 3H, $CH_2-C\underline{H}_3$), 2.95 (s, 3H, C2–CH_3), 3.12 (s, 3H, C1'–CH_3), 3.96 (s, 3H, N–CH_3), 4.9 (q, overlapping, 2H, $C\underline{H}_2-CH_3$), 7.55 (mc, overlapping, 2H, C-5-H, C6–H), 7.71 (mc, 1H, C7–H), 7.96 (mc, 1H, C4–H)
2e (400)	4.53 (s, 3H, OCH_3), 7.62 (mc, 2H, aromatic-H), 7.80 (mc, 5H, aromatic-H), 7.88 (mc, 1H, aromatic-H), 8.25 (mc, 1H, aromatic-H), 8.32 (d, ^3J = 4.3 Hz, 1H, aromatic-H), 11.60 (br. s, 1H, NH)
2f (200/–50 °C)	1.90 (s, 3H, C2–CH_3), 4.10 (s, 3H, OCH_3), 7.30–8.20 (m, 9H, aromatic-H), 11.40 (br. s, 1H, NH)
2f'	1.95 (s, 3H, C2–CH_3), 4.07 (s, 3H, OCH_3), 7.30–8.20 (m, 9H, aromatic-H), 11.40 (br. s, 1H, NH)

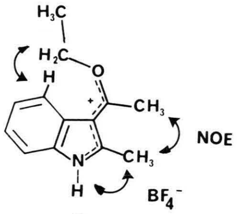
Table II. Barriers to EE/EZ-isomerization for **2**; ^1H NMR coalescence measurements.

Compound	T_c [K]	$\Delta G^{\neq}$ [kJ · mol^{-1}]
2a	<273	<65
2b	<273	<65
2c, 2c′	333	70.52[a]
2d, 2d′	328	69.75[a]
2e	<273	<65
2f, 2f′	293	67.2[b]

[a] 90 MHz spectrometer, CD_3NO_2; calculated from the coalescence of the OCH_2CH_3 resonances; [b] 200 MHz spectrometer, CD_2Cl_2; calculated from the coalescence of the OCH_3 resonances.

trimethinecyanine partial structure. As will be shown below, the position of the equilibrium in solution is sensitively controlled by the nature of the substituents on the indole moiety and/or at C-1′. The ^1H NMR spectra of **2a, 2b,** and **2e** at measurement temperatures between +20 and −90 °C in CD_2Cl_2 show, in accord with $^1H\{^1H\}$NOE experiments (see formula **2c** for the NOE's that confirm the conformation), that the conformational equilibrium lies completely to the side of the EE-isomers. In contrast, the cations of **2c,2c′** and **2d,2d′** at 20 °C, as well as **2f,2f′** at −50 °C give rise to doubled sets of signals. NOE measurements carried out in the region of the slow exchange indicate that equilibrium mixtures of the EE- and EZ-isomers are present in these cases. As can be seen from considerations of Büchi-Dreiding models, the populations of the two conformers are sufficiently large with respect to the ^1H NMR limits of detection as a consequence of the steric influence of the indole 2-methyl group (R^2) (EE/EZ ratio for **2c,2c′**, **2d,2d′** is approx. 1:1, for **2f,2f′** approx. 2:1).

With the aid of the Eyring equation [14], the barrier to rotation about the exocyclic C3/C1′ bonds in the unsymmetrical trimethine-cyanine partial structures of the respective isomeric mixtures **2c,2c′**, **2d,2d′**, and **2f,2f′** can be estimated from the coalescence temperatures T_c obtained by temperature dependent ^1H NMR measurements (Table II). The lower barrier to isomerization calculated for **2f,2f′** in comparison to **2c,2c′** and **2d,2d′** should, in the case of **2f,2f′**, be caused by a +M effect of the phenyl group which results in a reduction of the π-bond contribution to the exocyclic C3/C1′ bond.



2c

The most simple, experimental estimation of the extent of the charge delocalization in **2** and the resultant π-electron density at the C1′-center should be achieved by determination of the shift values of the carbon atoms of the conjugated trimethine chain in the ^{13}C NMR spectra [15, 16]. It is known that ^{13}C NMR data respond strongly to changes in the charge density and are influenced to a lesser degree by diamagnetic ring current effects [17]. The ^{13}C NMR shifts of the carbon atoms of the trimethine chains of **2a–2d′** are given in Table III (the assignments were made with the aid of fully coupled and *J*-modulated spin-echo spectra). At a measurement temperature of 20 °C, double sets of signals are also observed for the cations of **2c,2c′** and **2d,2d′** in the ^{13}C NMR spectra (in the case of **2f,2f′**, however, only at −55 °C). The hyperconjugative influence of the indole methyl group at C2 in **2c–2d′** exerts an effect

Table III. Selected 100.6 MHz ^{13}C NMR data of the tetrafluoroborates **2a–2d′** at 20 °C (δ scale, ppm, CD_3NO_2) and calculated relative charge densities at C1′ according to Ref. [16].

Compound	q_rC^+ at C1′	δ [ppm] C1′	C2	C3	C1′–CH_3	C2–CH_3	NCH_3	$OCH_2\underline{C}H_3$	$O\underline{C}H_2CH_3$
2a	0.493	197.6	150.6	139.8	20.0	–	–	14.8	73.7
2b	0.485	195.1	152.9	141.5	19.7	–	36.3	14.8	73.1
2c (EE)	0.484	194.7	163.3	138.5	20.9	19.1	–	14.9	72.5
2c′ (EZ)	0.484	194.7	164.2	137.6	20.2	18.5	–	14.9	72.3
2d (EE)	0.479	193.1	164.1	141.2	21.0	16.8	32.4	14.9	72.0
2d′ (EZ)	0.478	192.9	163.1	140.4	20.4	16.3	32.8	14.9	72.0

on the chemical shifts of the C1′-centers. When the recognized relationship between ^{13}C NMR chemical shifts and the relative charge densities at cationic centers is applied [16, 17], in these cases a *decrease* in the positive charge (q_rC^+) at C1′ with the increasing introduction of methyl groups on to the indole skeleton is observed as a result of hyperconjugative effects (Table III).

The ^{13}C NMR spectra of the phenyl-substituted cations of **2e** and **2f, 2f′** (C1′ of **2e** = 193.1 ppm, of **2f, 2f′** = 190.2 ppm in CD_2Cl_2) exhibit similar behaviour. The influence of the +M effect of the phenyl group on the charge density at C1′ is relatively small in comparison to that of the methyl-substituted cations. Considerations of Büchi-Dreiding molecular models show that a fully coplanar arrangement of the phenyl rings in **2e, 2f, 2f′** to the trimethine chains should be rendered difficult by steric effects (see also the X-ray structural analysis of **2e**).

Table IV. π-Bonding orders P_π of indole, **2c, 2c′, 2d, 2d′**, and **2f, 2f′** as estimated from ^{13}C NMR chemical shift data. (The estimations were made according to Ref. [18] from the C3 shift differences of 2-methylated and 2-unsubstituted compound pairs of **2**.)

Compound	P_π (C2−C3)
Indole	0.812
2c	0.747
2c′	0.795
2d	0.693
2d′	0.736
2f, 2f′	0.750

It is known that the π-bonding order of π-systems (*e.g.*, the $H_3C-C\alpha=C\beta$-system) can be calculated on the basis of the β-effect of methyl groups on the ^{13}C NMR chemical shifts of neighbouring carbon atoms using the simple relationship [18]:

$$^{\Delta\delta}C\beta[\mathrm{ppm}] = 12.6 - 18.6\ P_\pi.$$

The estimated π-bond orders (P_π) of the indole C2/C3 bonds of **2** thus estimated from the shift differences are given in Table IV. In comparison to the value for indole, the double bond character of the indole 2/3 bond in the cations **2** is reduced as a consequence of the mesomerism of the trimethine-cyanine structure.

Table V. Experimental data for the crystal structure determination of compound **2e**.

Crystal data	
Formula	$C_{16}H_{14}NOBF_4$
Relative molecular mass	323.10
Crystal dimensions	approx. 0.7×0.2×0.18 mm
Absorption	$\mu = 10.3\ \mathrm{cm}^{-1}$, no correction
Space group	Cc, $Z = 4$
Lattice constants	$a = 796.4(3)$ pm $b = 1280.2(4)$ pm, $\beta = 91.99(2)°$ $c = 1471.2(1)$ pm
Temperature	293 K
Density	$d_c = 1.432\ \mathrm{g \cdot cm^{-3}}$
Data collection	
Diffractometer	4-circle, CAD4 (Enraf-Nonius)
Radiation	$Cu-K_\alpha$, graphite monochromator
Scan type	ω-scan
Scan width	$(1.6 + 0.08\ \mathrm{tg}\theta)$ 0 and 25% on the left-hand and right-hand side of a reflection for background determination
Measuring range	$2° < \theta > 60°$, $\pm h$, $\pm k$, $\pm l$
Reflections	4302, 2083 unique with $F_o > 3\sigma(F_o)$
Computing	
Computer	Sperry 1100/62 at the HRZ Marburg
Programs	System STRUX [21] with SHELXS86 [22], SHELX76 [23] and ORTEP [24]
Atomic scattering factors for neutral atoms [25]	
Anomalous dispersion included [26]	
Refinement	block diagonal matrix least squares, $\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$ minimalized
R values	$R = 0.038$, $R_w = 0.036$, $R_g = wR = 0.039$
Max. parameter shift	0.03 · e.s.d.
$\Delta\varrho$ max., min.	0.24, −0.29 e/Å

Conformation of **2e** *in the crystal state*

Of the series of indolyl-stabilized carbenium ions **2,** we were able to obtain **2e** in the form of single crystals and, therefore, were able to carry out the first X-ray crystal structure analysis of a representative of this class of compounds. The crystal and experimental data are compiled in Table V, the resulting atomic parameters in Table VI, and bond lengths and angles in Table VII*.

The cation of **2e** in the crystal state exhibits axial chirality and exists exclusively in the EE-basic configuration; this is in good agreement with the low temperature ^{1}H NMR measurements and an NOE experiment.

The cation of **2e** exists in racemic form; the entire indole moiety and the C10 atom are practically in a plane (maximum deviation 0.012 Å), from which the O-atom, however, protrudes by 0.295 Å from the side opposite to C17, while the methyl C11 atom lies only 0.089 Å above this. The phenyl ring is tilted to this plane by 60.0(1)°. The torsional angle C3−C10−C12−C17 amounts to 50.7(4)°; thus, the major contribution to the interplanar angle is attributed to a twisting about the C10−C12 axis and the rest to a tilting of the C10−C12 bond by 9.5(2)° away from the indole plane. This bond, in turn, is bent only by 2.0(2)° away from the phenyl plane on the C3 side.

Table VI. Atomic parameters and equivalent isotropic temperature factors for compound **2e** with estimated standard deviations in parentheses.

Atom	x	y	z	U_{eq}
O	0.46210(0)	0.2609(2)	0.12120	0.0526(6)
N1	0.3733(4)	−0.0751(2)	0.1884(2)	0.0533(8)
C2	0.4326(4)	−0.0195(2)	0.1216(3)	0.051(1)
C3	0.4088(4)	0.0874(2)	0.1392(2)	0.047(1)
C4	0.2697(4)	0.1735(3)	0.2803(2)	0.051(1)
C5	0.1933(4)	0.1472(3)	0.3599(2)	0.060(1)
C6	0.1738(5)	0.0444(3)	0.3862(2)	0.062(1)
C7	0.2284(4)	−0.0366(3)	0.3342(2)	0.059(1)
C8	0.3060(4)	−0.0101(2)	0.2543(2)	0.0482(9)
C9	0.3275(4)	0.0929(2)	0.2265(2)	0.0450(9)
C10	0.4625(4)	0.1681(2)	0.0838(2)	0.048(1)
C11	0.4789(6)	0.3576(2)	0.0681(3)	0.060(1)
C12	0.5186(4)	0.1503(2)	−0.0086(2)	0.0477(9)
C13	0.6752(4)	0.1871(2)	−0.0353(2)	0.054(1)
C14	0.7282(5)	0.1655(3)	−0.1210(2)	0.061(1)
C15	0.6294(5)	0.1097(3)	−0.1821(2)	0.064(1)
C16	0.4734(5)	0.0738(3)	−0.1563(2)	0.069(1)
C17	0.4195(5)	0.0928(2)	−0.0701(2)	0.059(1)
B1	0.9994(4)	0.3347(2)	0.1177(2)	0.054(1)
F1	0.8884(3)	0.2908(1)	0.1786(1)	0.0854(7)
F2	1.0774(2)	0.2529(1)	0.0748(1)	0.0733(6)
F3	0.9081(3)	0.3925(2)	0.0552(1)	0.0879(7)
F4	1.1145(3)	0.3962(2)	0.1627(2)	0.0930(7)

Table VII. Bond lengths [Å] and bond angles [°] in compound **2e** with estimated standard deviations in parentheses.

O−C10	1.309(3)	O−C11	1.472(4)	N1−C2	1.315(5)
N1−C8	1.399(4)	C2−C3	1.406(4)	C3−C10	1.392(4)
C3−C9	1.461(4)	C4−C5	1.379(5)	C4−C9	1.388(4)
C5−C6	1.382(5)	C6−C7	1.369(5)	C7−C8	1.389(5)
C8−C9	1.393(4)	C10−C12	1.464(4)	C12−C13	1.402(5)
C12−C17	1.389(4)	C13−C14	1.372(5)	C14−C15	1.373(5)
C15−C16	1.390(5)	C16−C17	1.375(5)		
F1−B1	1.398(4)	F2−B1	1.381(4)	F3−B1	1.369(4)
F4−B1	1.363(4)				
C10−O−C11	122.6(2)	C2−N1−C8	110.6(3)	C3−C2−N1	109.6(3)
C10−C3−C2	124.6(3)	C10−C3−C9	129.3(3)	C2−C3−C9	106.0(3)
C5−C4−C9	117.9(3)	C6−C5−C4	121.8(3)	C7−C6−C5	121.6(3)
C8−C7−C6	116.6(3)	N1−C8−C9	107.8(3)	N1−C8−C7	129.3(3)
C9−C8−C7	122.8(3)	C3−C9−C4	134.7(3)	C3−C9−C8	105.9(3)
C4−C9−C8	119.3(3)	O−C10−C3	115.0(3)	O−C10−C12	122.4(2)
C3−C10−C12	122.5(3)	C10−C12−C13	120.7(3)	C10−C12−C17	120.1(3)
C13−C12−C17	119.1(3)	C12−C13−C14	119.6(3)	C13−C14−C15	121.3(3)
C14−C15−C16	119.3(3)	C15−C16−C17	120.3(3)	C12−C17−C16	120.3(3)
F1−B1−F2	107.0(2)	F1−B1−F3	108.3(3)	F1−B1−F4	110.5(3)
F2−B1−F3	109.8(3)	F2−B1−F4	110.8(3)	F3−B1−F4	110.3(2)

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* Further details of the crystal structure analysis can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG, by quoting the deposition number CSD 53778, the names of the authors, and the journal reference.

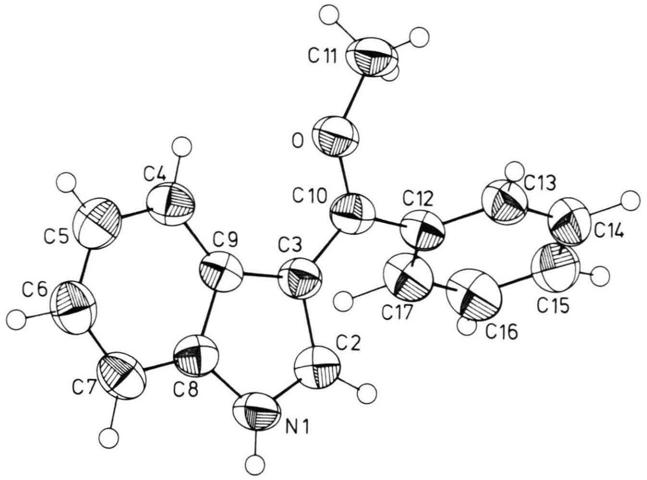

Fig. 1. ORTEP drawing of the cation of **2e** in the crystal state. Thermal ellipsoids at the 50% probability level. Hydrogen atoms are represented by spheres of arbitrary size. (The numbering scheme is not consistent with the IUPAC nomenclature rules.)

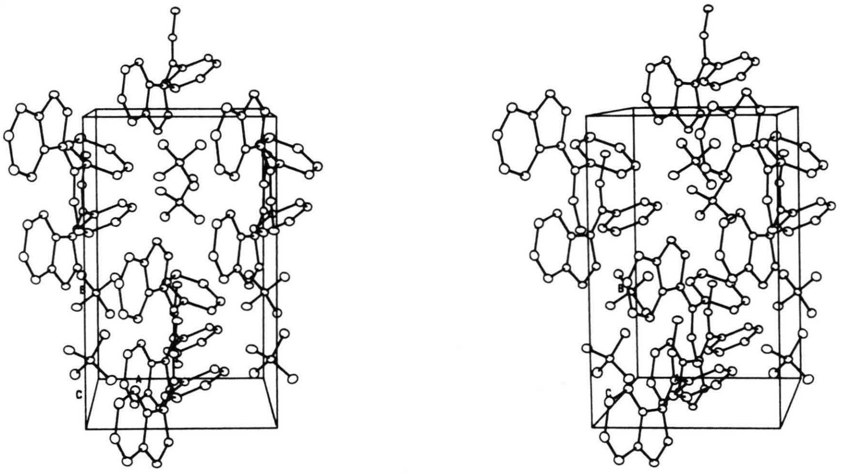

Fig. 2. Stereoscopic view of the unit cell of compound **2e.**

The axial chirality of the cation in the crystalline state is attributable to a propeller conformation [19]. The reference plane of the propeller is formed, according to Mislow [19], by the atoms C3, C10, C12, and O. The phenyl group is twisted by 50.7° with respect to this plane and the indole moiety by 11°. In the mesomeric trimethine-cyanine chain, the N1–C2, C3–C10, and C10–O bonds are significantly shortened (Table VII) and thus exhibit a considerable amount of double bond character. In contrast, the C2–C3 bond in **2e** is noticeably longer than that in the parent indole (C2–C3 = 1.34 Å) [6, 20]. Thus, the X-ray structural analysis confirms the lower π-bonding order of the C2–C3 bond in this cation **2e** as already estimated from the ^{13}C NMR chemical shifts (Table IV).

Experimental

Procedures for the preparation and further physical data of compounds **2** (yields: 25–90%) are given in Refs. [10–13, 27].

^{1}H NMR spectra: Bruker WH 90, Bruker AC 200, Bruker WM 400 spectrometers; ^{13}C NMR spectra: Bruker WM 400 (δ scale, TMS as internal standard).

The crystallization of **2e** was achieved by allowing the mother liquor in dichloromethane/diethyl ether to stand for 10 weeks.

Experimental details of the performance of the X-ray structural analysis are given in Table V.

We thank the Deutsche Forschungsgemeinschaft (Bonn) and the Fonds der Chemischen Industrie for financial support of this work.

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