Dipole moments of 9-alkylcarbazoles 3-substituted with double-bonded groups

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Syntheses of 9-alkyl-3-phenylazocarbazole and its analogues containing azomethine and ethylene bridges were described. The dipole moments of these compounds were measured in benzene solutions and compared with those of 9,9'-diethyl-3,3'-azocarbazole and 9-methyl-3-carbazolylazonitrile. Explanations of very high dipole moment of the azocarbazole and the ease of the thermal transition of its *cis* to *trans* isomer are proposed.

В настоящей статье представлен синтез 9-алкил-3-фенилазокар-базола и его аналогов содержащих азометиновый или этиленовый мостик. Экспериментально были найдены дипольные моменты этих соединений и сопоставлены с дипольными моментами 9,9'-диэтил-3,3'--азокарбазола и 9-метил-3-карбазолилазонитрила. Предложено объяснение ненормально высокого числового показателя дипольного момента азокарбазола и тенденции подвергаться термическому переходу его *цис* изомера на *транс* изомер.

9,9'-Diethyl-3,3'-azocarbazole exhibits unusually high dipole moment $(4.47 \times 10^{-30} \text{ C m})$, significantly higher than *e.g.* 2,2'-azonaphthalene $(3.57 \times 10^{-30} \text{ C m})$ [1]. Provisional explanation based on the conformational analysis seems to be inappropriate [2]. Asymmetrical conformations may be responsible for the dipole moments of azoquinolines, 2,2'- and 3,3'-azopyridines [3, 4] but such an explanation is inadequate in the case of azobenzene and 4,4'-azopyridine [4, 5]. Recent investigations on the influence of 3-substituents on the magnitude and direction of the dipole moments of carbazole derivatives pointed out that both factors are dependent upon the conjugation of the pyrrole nitrogen lone pair with a substituent. Consequently, strongly withdrawing groups as NO_2, CN, N_2Ar dispose the dipole moment vector nearly parallel to the N-9-ring-substituent axis [6]. Hence the dipole moment of 9,9'-diethyl-3,3'--azocarbazole should be nearly equal to zero regardless of the polarization of the both carbazole systems and conformation of the molecule.

$$\mu = 4.37 \times 10^{-30} \text{ C m}$$
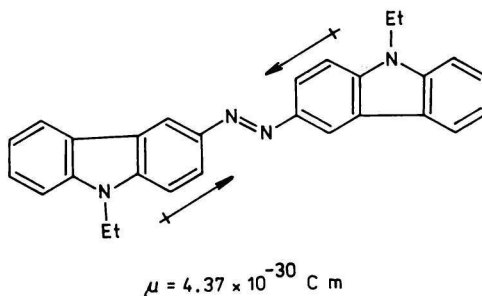
Dipolometric and spectroscopic data on the 4,4′-disubstituted azobenzenes indicate that the azo bridge may contribute to the dipole moment of the azo molecule especially in the presence of donating substituents in conjugated positions [7]. In the case of 9,9′-diethyl-3,3′-azocarbazole a strong conjugation should be expected due to the geometry of the carbazole molecule which prefers the trigonal (sp^2) hybridization of the pyrrole nitrogen.

In the present paper we wish to report on the dipolometric measurements of some 3-substituted 9-alkylcarbazoles containing double-bonded groups.

Ia—IVd
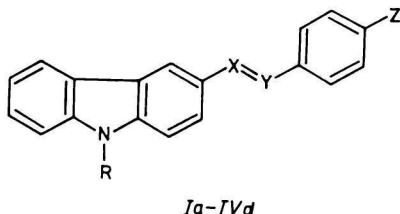
These derivatives were designed as the model compounds for elucidation of the source of the dipole moment of the azocarbazole molecule.

Experimental

The dipole moments of the aforesaid carbazole derivatives were measured in benzene solutions at 25 °C by the standard procedure described in the previous paper [6]. Calculations were done employing the Halverstrand—Kumler method.

3-(4-Bromobenzylidenamino)-9-ethylcarbazole

3-Amino-9-ethylcarbazole (4.20 g; 0.02 mol) and 4-bromobenzaldehyde (4.10 g; 10 % excess) were dissolved in 80 cm³ of boiling, absolute ethanol. A drop of boron trifluoride etherate was added and the orange solution was slowly cooled. The crude product was collected by filtration and crystallized from isooctane boiling with charcoal and the title

compound was isolated (6.18 g, 82 %) as light yellow prisms, m.p. = 108—109 °C. For $C_{21}H_7N_2Br$ w_i(calc.): 66.12 % C, 4.16 % H; w_i(found): 66.24 % C, 4.26 % H. ^1H NMR spectrum (CDCl$_3$), δ/ppm: 8.51 (s, 1H, methine proton), 8.2 (d, $^3J = 8$ Hz, 1H, H-5 of carbazole system), 7.90 (d, $^4J = 2$ Hz, 1H, H-4), 7.78 and 7.51 (d, $^3J = 9$ Hz, protons of benzene ring), 7.14—7.42 (m, 5H, remaining aromatic protons), 4.21 (q, $^3J = 7$ Hz, 2H), and 1.27 (t, $^3J = 7$ Hz, 3H, N-ethyl group). Other azomethines were obtained analogously from 3-amino-9-ethylcarbazole and 3-formyl-9-methylcarbazole.

9-Ethylcarbazolyl-3-azonitrile

3-Amino-9-ethylcarbazole (8.41 g; 0.04 mol) was diazotized in 3 M-HCl at 0—5 °C with sodium nitrite (0.05 mol), the solution of diazonium salt was neutralized with sodium acetate and treated with sodium cyanide (4.90 g). The precipitate was collected with methylene chloride, the extract was washed with water and dried with magnesium sulfate. The solution was concentrated to 100 cm^3 refluxed for 1 h, diluted with 100 cm^3 of n-hexane and left for crystallization. The product (4.30 g, 43 %) was obtained as brick-red prisms melting at 147—150 °C with decomposition. For $C_{15}H_{12}N_4$ w_i(calc.): 72.56 % C, 4.87 % H; w_i(found): 72.69 % C, 4.90 % H. IR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 730, 745, 800 (in phase, out-of-plane hydrogen wagging), 1450, 1470 (alkyl group deformations), 2160 ν(CN), 2870, 2930, 2965, 3060 ν(CH). ^1H NMR spectrum (CDCl$_3$), δ/ppm: 8.52 (d, $^4J = 2$ Hz, 1H, H-4), 8.00 (dd, $^4J = 2$ Hz, $^3J = 9$ Hz, 1H, H-5), 7.73 (dd, $^4J = 2$ Hz, $^3J = 9$ Hz, 1H, H-2), 7.05—7.47 (m, 4H, remaining aromatic protons), 4.20 (q, $^3J = 7$ Hz, 2H) and 1.02 (t, $^3J = 7$ Hz, 3H, 9-ethyl group).

3-Phenylazo-9-methylcarbazole

3-Aminocarbazole (7.30 g; 0.04 mol) and nitrosobenzene (4.28 g; 0.04 mol) were dissolved in 100 cm^3 of methanol—acetic acid ($\varphi_r = 1 : 1$). The solution was stirred for 0.3 h at room temperature, silica gel (70 g) was added and the solvent evaporated in vacuum. The product was eluted with toluene, the solution concentrated and cooled. Crude 3-phenylazocarbazole (4.90 g, 45 %) with m.p. = 202—204 °C was collected by filtration. Recrystallization from benzene—hexane gave 4.50 g (41 %) of pure product with m.p. = 209—210 °C.

3-Phenylazocarbazole (4.07 g; 15 mmol) and methyl iodide (1.9 cm^3, 30 mmol) were dissolved in 80 cm^3 of dimethyl sulfoxide. Tetrabutylammonium bromide (50 mg) and aqueous solution of potassium hydroxide (50 %, 20 cm^3) were added and the mixture was intensely stirred for 0.5 h. The orange precipitate was collected by filtration, washed with water and crystallized from methanol. The product was obtained in 79 % yield, m.p. = 131—133 °C. Recrystallization from isooctane gave 3.15 g (73 %) of long, orange needles melting at 135—136 °C. For $C_{19}H_{15}N_3$ w_i(calc.): 79.97 % C, 5.30 % H; w_i(found): 80.08 % C, 5.40 % H. IR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 680 (phenyl ring bend), 735, 760, 810, 890 (aromatic CH deformations), 1420 (methyl group deformations), 3040 (aromatic CH stretching vibrations).

ω-(9-Methyl-3-carbazolyl)styrene

3-Formyl-9-methylcarbazole (4.18 g; 0.02 mol) and benzyltriphenylphosphonium bromide (9.55 g, 10 % excess) were dissolved in 100 cm³ of dimethyl sulfoxide. Sodium amide (1.56 g; 0.04 mol) was added and the mixture stirred at 40 °C for *ca.* 20 min until the orange colour ceased. The crude product was precipitated with water, washed with hot methanol to remove triphenylphosphine oxide, and crystallized from the methylene chloride—hexane mixture. *trans*-ω-(9-Methyl-3-carbazolyl)styrene was obtained in 64 % yield (3.62 g) as long, colourless needles, m.p. = 153—154 °C with polymorphic change at 135 °C. For $C_{21}H_{17}N$ w_i(calc.): 89.00 % C, 6.05 % H; w_i(found): 89.11 % C, 6.17 % H. IR spectrum (KBr), $\tilde{v}/cm^{-1}$: 690, 745, 800, 805 (phenyl ring bending and aromatic CH deformations), 960 (olefinic *trans*-CH wagging), 1625 (C=C stretch), 3030, 3050 (olefinic and aromatic CH stretching vibrations).

From the concentrated and cooled to −20 °C mother liquors the second isomer was isolated as lemon-yellow prisms, m.p. = 113—115 °C. Recrystallization from isooctane gave 1.53 g (27 %) of *cis*-ω-(9-methyl-3-carbazolyl)styrene; m.p. = 116—117 °C. For $C_{21}H_{17}N$ w_i(calc.): 89.00 % C, 6.05 % H; w_i(found): 89.07 % C, 6.19 % H. IR spectrum (KBr), $\tilde{v}/cm^{-1}$: 690, 740, 770, 800, 825 (phenyl ring bend and out-of-plane hydrogen wagging), 710, 1395 (olefinic *cis*-CH wagging and rocking vibrations), 1625 (C=C stretch), 3000, 3050 (olefinic and aromatic CH stretching vibrations). ¹H NMR spectrum (CDCl₃). δ/ppm: 8.00 (d, ^4J = 2 Hz, 1H, H-4 of carbazole system), 7.29 (d, ^3J = 8 Hz, 1H, H-5), 7.10—7.50 (m, 10H, remaining aromatic protons), 6.85 (d, ^3J = 12 Hz, 1H) and 6.60 (d, ^3J = 12 Hz, 1H, olefinic protons), 3.60 (s, 3H, *N*-methyl group).

Results and discussion

Carbazole derivatives containing azomethine group (*Ia—IIb*) were obtained from 3-formyl- and 3-amino-9-alkylcarbazole by condensation with aniline and benzaldehyde, respectively. 3-Nitrosocarbazole and aniline formed 3-phenyl-azocarbazole (*IVa*) in very poor yield; condensation of 3-aminocarbazole with nitrosobenzene gave better results. Azonitriles *Va*, *Vb* were prepared from diazotized 3-aminocarbazoles by coupling with cyanide anion according to *Le Fèvre* and *Vine* [8, 9]. Labile *cis* isomers were detected by TLC in crude reaction mixtures but could not be isolated in a pure state due to their rapid conversion to *trans* azonitriles at room temperature and higher solubility.

Wittig reaction carried out on 3-formyl-9-methylcarbazole with the use of benzyltrimethylphosphonium chloride gave the mixture of corresponding stilbenes (*IIIa*, *IIIb*). The isomers were separated by fractional crystallization. The *trans* configuration was assigned to the less soluble isomer *IIIa* which displays in its IR spectrum a strong band at $\tilde{v}$ = 960 cm⁻¹, characteristic of *trans* olefinic protons [10]. In the ¹H NMR spectra of stilbenes the signals of olefinic protons are observed at δ = 7.10 ppm in *trans* and at δ = 6.55 ppm in *cis* isomer [11], hence the spectrum of *IIIa* is illegible due to the overlap of aromatic and olefinic

Table 1

Substituted 9-alkylcarbazoles with double-bonded groups

Compound	R	X	Y	Z	Yield %	M.p. °C	Mass spectra, m/z (I_r/%)
Ia	Me	CH	N	H	80	128—129	284 (M^+, 100), 283 (62), 268 (6), 206 (6), 181 (13), 153 (6), 135 (6), 77 (10)
Ib	Me	CH	N	Br	87	175—177	364 (100), 362 (M^+, 97), 284 (13), 269 (15), 205 (57), 180 (48), 155 (55)
IIa	Et	N	CH	H	73	99—100	298 (M^+, 100), 283 (39), 269 (9), 179 (8), 165 (3), 152 (3)
IIb	Et	N	CH	Br	82	108—109	378 (94), 376 (M^+, 100), 363 (29), 361 (29), 297 (5), 281 (6), 179 (19), 178 (17)
IIIa	Me	CH	CH	H	64	153—154	283 (M^+, 100), 282 (18), 281 (8), 267 (21), 142 (2), 141 (4), 81 (11), 77 (3)
IIIb	Me	CH	CH	H	27	116—117	283 (M^+, 100), 282 (19), 281 (9), 267 (22), 180 (3), 77 (4)
IVa	H	N	N	H	41	209—210	271 (M^+, 33), 194 (6), 166 (100), 139 (26), 77 (18)
IVb	Me	N	N	H	73	135—136	285 (M^+, 30), 208 (3), 180 (100), 152 (26), 151 (8), 77 (19)
IVc	Et	N	N	H	64	39—40	299 (M^+, 29), 222 (3), 194 (100), 179 (44), 164 (5), 152 (6), 77 (21)
IVd	H	N	N	Br	16	265—266	351 (12), 349 (M^+, 11), 166 (100), 157 (9), 155 (6), 139 (31), 57 (14), 55 (13)
Va	3-Carbazolylazonitrile				39	> 300	220 (M^+, 28), 192 (14), 182 (12), 166 (100), 140 (19), 139 (42), 29 (6)
Vb	9-Ethylcarbazolyl-3-azonitrile				43	147—150	248 (M^+, 51), 194 (100), 193 (5), 179 (37), 165 (12), 29 (37)

protons. *cis-ω-(9-Methyl-3-carbazolyl)styrene* (*IIIb*) gives two doublets at $\delta = 6.85$ and 6.60 ppm with the coupling constant of 12 Hz indicative of *cis* configuration [12]. The most compelling evidence of the assignment comes from the isomerization experiment [13]. The solution of *IIIa* in methylene chloride treated with hydrogen bromide gives *IIIb* in 80 % yield. Since the reaction can be followed by TLC (benzene—isooctane—butanone, $R_f = 0.39$ and 0.46 for *IIIa* and *IIIb*, resp.) the reversibility of the isomerization can be observed. After 4 h at room temperature both the compounds produce an equilibrium mixture in which *IIIa* prevails. All the compounds prepared are listed in Table 1.

The auxiliary parameters and final results (μ_{exp}) are collected in Table 2. The slopes of the plots of the relative permittivity, refractive index, specific volume, and density *vs.* solute mole fraction are denoted a_ε, a_n, a_v, and a_ϱ, respectively. The remaining symbols have the usual meaning.

Table 2

Dipole moments μ_{exp} of 9-alkylcarbazole derivatives (in benzene)

Compound	a_ε	a_n	a_v	a_ϱ	P_{2x}	R_D	$\mu_{exp}/(10^{-30}\,C\,m)$
Ia	3.74	0.53	−0.33	0.26	268.70	96.31	9.57 ± 0.13
Ib	6.24	0.57	−0.48	0.37	498.50	110.50	14.33 ± 0.13
IIa	2.22	0.58	−0.28	0.21	201.60	109.30	6.87 ± 0.07
IIb	3.64	0.56	−0.40	0.30	341.90	123.60	10.74 ± 0.10
IIIa	2.22	0.60	−0.26	0.20	193.00	105.90	6.67 ± 0.07
IVb	2.80	0.80	−0.32	0.24	220.40	112.50	7.47 ± 0.07
Vb	28.86	0.94	−0.27	0.21	1413.00	108.40	26.60 ± 0.10

Dipole moments of *IIa*, *IIIa*, and *IVb* exceed that of 9-ethylcarbazole by less than 1.67×10^{-30} C m and increase slightly with the electron-withdrawing character of the X=Y bridge.
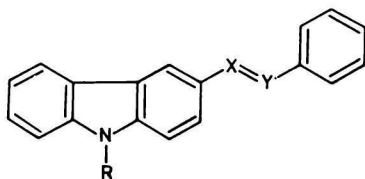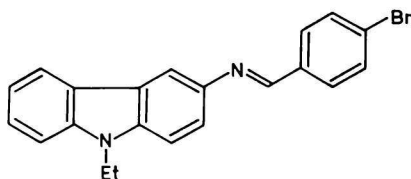

	X = Y	
IIIa	CH=CH	$\mu = 6.67 \times 10^{-30}$ C m
IIa	N=CH	$\mu = 6.87 \times 10^{-30}$ C m
IVb	N=N	$\mu = 7.47 \times 10^{-30}$ C m

3-Bromo-9-ethylcarbazole and *IIb* display nearly the same dipole moments.
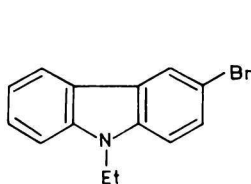
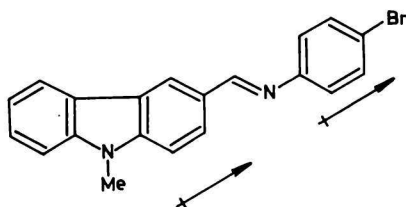$\mu = 11.01 \times 10^{-30}$ C m

IIb, $\mu = 10.74 \times 10^{-30}$ C m

The algebraic sum of the dipole moments of *Ia* and bromobenzene is equal to that of *Ib* within an experimental error.

*Ib*, $\mu = 14.33 \times 10^{-30}$ C m

It has been shown in the previous paper [6] that dipole moments of simple carbazole derivatives are determined with the distribution of the nitrogen lone pair. Consequently its magnitude and direction is strongly influenced with the conjugation between pyrrole nitrogen and a substituent in *para* position. The same explanation can be adopted for the aforementioned observations: electron-withdrawing substituents increase the dipole moment of the carbazole system and change its direction towards N-9—C-3 axis.

Dipole moment of *Vb* is very high and exceeds that of 3-cyano-9-ethylcarbazole by 7.35×10^{-30} C m. Analogous differences within the benzene [14, 15] and biphenyl [16, 17] series are significantly lower. The result is indicative of the polarizability of the carbazole system and electron-withdrawing properties of the azonitrile group. Consequently one can assume that the vectors of the cyano group and carbazole system are collinear and consider the algebraic difference $(26.60 \times 10^{-30} - 19.25 \times 10^{-30})$ as the contribution of the azo bridge to the dipole moment of *Vb*. The calculated value is in agreement with the experimental dipole moment of *IVb*.

IVb, $\mu = 7.47 \times 10^{-30}$ C m
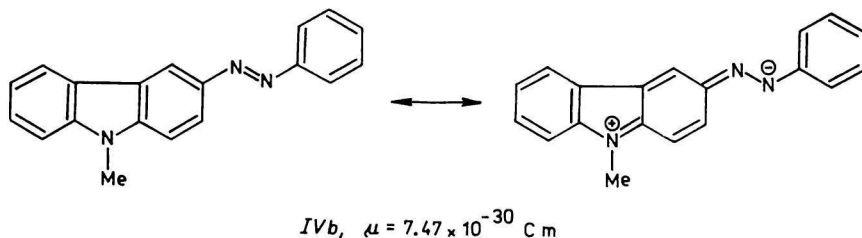
Analogous mesomeric structure with separated charges may contribute significantly to the resonance hybrid of 9,9'-diethyl-3,3'-azocarbazole. Assuming a typical geometry of carbazole system and the azo bridge, and free rotation around the Ar—N bond, the dipole moment of the hypothetical structure can be evaluated for 4.57×10^{-30} C m.
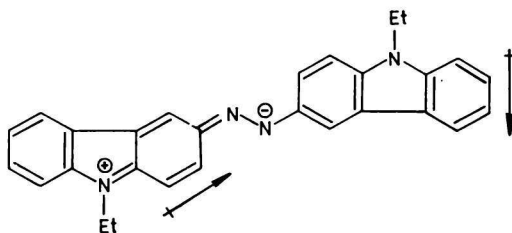
The experimental value is 4.37×10^{-30} C m [2]; this coincidence may be fortuitous but it supports our views on the source of the dipole moment of symmetrical azo compounds. Contribution of the polar mesomeric structures to a resonance hybrid makes the molecule nonplanar due to the hybridization of azo nitrogens intermediary between the sp^2 and sp^3 states. Consequently, there are two possible conformations: the one is centrosymmetric but the other has a dipole moment dependent on the extent and polarizability of the aromatic system.

The symmetric azoarenes displaying high dipole moments do not form stable *cis* isomers. The mechanism of the thermal transition of *cis* to *trans* isomer of azobenzenes remains obscure. Inversion mechanism is generally accepted [18] for azobenzene itself, however *Asano* [19] advocated that it changes from inversion in hexane to rotation in polar solvents. Isomerization *via* dipolar rotational transition state is also preferred for push-pull azobenzenes [19, 20]. Since the alternative: inversion or rotation is still unresolved it is probably incorrectly formulated. If we assume that in the transition state the charge distribution is approximated with the polar mesomeric structure, the distinction between inversion and rotation becomes meaningless. Such an interpretation accounts for the influence of solvents and substituents on the rate of isomeriza-

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tion [21] and rapid transformation of *cis*-9,9'-diethyl-3,3'-azocarbazole at room temperature [22].

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