

The dipole moments of carbazole derivatives

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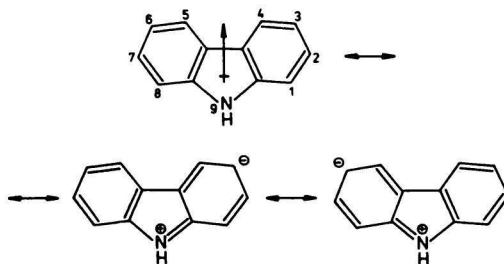
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Dipole moments of twenty 3-substituted and 3,6-disubstituted derivatives of 9-alkylcarbazoles have been measured. Discussion on the influence of substituents on the dipole moments led to the conclusion that distribution of the electron density of lone electron pair of the pyrrole nitrogen determines the dipole moments of carbazole derivatives.

Экспериментально найдены дипольные моменты 20 3-замещенных и 3,6-дизамещенных производных 9-алкилкарбазолов. Исследование влияния заместителей на величину дипольных моментов показало, что распределение электронной плотности свободной пары электронов пирролового атома азота определяет величину и направление дипольных моментов производных карбазолов.

Measurements of dipole moments are frequently applied to stereochemical problems. Our work stems from the studies on the configuration and conformation of 9,9'-diethyl-3,3'-azocarbazole [1]. The *Z* configuration for the stable isomer has been ruled out however a large value of the dipole moment (4.37×10^{-30} Cm) merits further investigation. Our aim was to elucidate the influence of various substituents on the charge distribution in the carbazole system by estimation of the dipole moments of 3-substituted and 3,6-disubstituted 9-alkylcarbazoles.



Scheme 1

The dipole moment of carbazole (6.97×10^{-30} Cm) is significantly higher than that of diphenylamine (3.34×10^{-30} Cm) [2]; it is oriented with the positive end towards the nitrogen atom as shown in Scheme 1. Probably planar and rigid heterocyclic system facilitates conjugation between pyrrole nitrogen and carbocyclic rings. The polar N—H bond also contributes since the dipole moment of 9-ethylcarbazole is lower (5.80×10^{-30} Cm); within the halocarbazole series a similar difference ($\mu = (0.33\text{—}1.00) \times 10^{-30}$ Cm) is observed [3]. The 9-alkyl group increases solubility of carbazoles in benzene and makes the measurements of dipole moments of nitro and amino derivatives possible at room temperature.

Experimental

Halo derivatives of carbazole were obtained according to the previously published procedures [4—6]. Preparation of aminocarbazoles and their derivatives has been also described elsewhere [7, 8]. 3-Azido-9-ethylcarbazole (yellow prisms from n-hexane, m.p. = 53—56°C with decomposition) was prepared from the corresponding amine according to the procedure described by *Sawicki* [9]. 3-Acetyl-9-ethylcarbazole (m.p. = 110—111°C, from methanol) and 3,6-diacetyl-9-ethylcarbazole (m.p. = 182—183°C, from toluene) were obtained by the Friedel—Crafts acetylation of 9-ethylcarbazole according to the literature data [10, 11]. The Vilsmeier—Haack formylation [12] of 9-methylcarbazole gave 3-formyl derivative (m.p. = 79—80°C, from methanol); condensation with hydroxylamine in ethanol solution yielded the oxime (m.p. = 211—213°C, decomp., from ethanol). 3-Formyl-9-methylcarbazole was reduced employing the Wolff—Kishner method to 3,9-dimethylcarbazole (m.p. = 85—86°C, from n-hexane, picrate: maroon needles m.p. = 134—135°C). Further formylation with subsequent reduction gave 3,6,9-trimethylcarbazole (m.p. = 110—111°C, from n-hexane, picrate: brown needles m.p. = 152—153°C).

The measurements were carried out in benzene solutions at 25°C. Relative permittivities were estimated using Dipolmeter DMO1 (WTW, Germany). The procedure of handling the samples was the same as described earlier [13]. For each series six solutions were prepared in the mass fraction from 10^{-3} to 6×10^{-3} . The data given in Table 1 are average values of three independent determinations. The meaning of the coefficients a_ϵ , a_n , and a_ρ is given by the formulas: $\epsilon_{12} = \epsilon_1(1 + a_\epsilon x)$; $n_{12}^2 = n_1^2(1 + a_n x)$ and $\rho_{12} = \rho_1(1 + a_\rho x)$ where ϵ , n , ρ , and x denote the relative permittivity, the sodium D-line refractive index, the density, and the solute mole fraction, respectively. The solvent values are specified by the subscript 1, while those of the solutions by 12. Dipole moments were calculated employing the methods of Halverstrand—Kumler, Le Fèvre—Vine and Hedestrand, the results were nearly the same regardless of the method used. The computer Odra 1305 (Elwro, Poland) was used for the least-square curve fitting and for all other computations.

Table 1

Auxiliary parameters for calculations of the dipole moments of 9-alkylcarbazoles derivatives according to the Halverstrand—Kumler method

	Substituents						$\mu_{\text{exp}}/(10^{-30}\text{Cm})$			
	9	3	6	a_c	a_n	a_v		a_q	$P_{2,sc}$	R_D
Et	H	H	H	2.20	0.44	-0.22	0.17	134.60	69.24	5.80 ± 0.13
Me	NMe ₂	H	H	1.64	0.51	-0.29	0.22	126.30	78.09	4.90 ± 0.37
Me	NMe ₂	NMe ₂	NMe ₂	0.98	0.49	-0.33	0.25	114.30	89.39	3.34 ± 0.50
Et	NH ₂	H	H	2.26	0.47	-0.26	0.20	144.40	73.25	6.07 ± 0.03
n-Hex	NH ₂	NH ₂	NH ₂	1.63	0.42	-0.22	0.17	163.20	98.73	5.70 ± 0.20
Me	Me	H	H	1.78	0.41	-0.24	0.18	118.20	67.29	5.10 ± 0.10
Me	Me	Me	Me	1.36	0.34	-0.21	0.16	111.90	71.20	4.50 ± 0.07
Et	Cl	H	H	5.44	0.42	-0.31	0.24	290.80	74.45	10.43 ± 0.10
Et	Cl	Cl	Cl	6.82	0.35	-0.36	0.28	400.30	78.18	13.18 ± 0.10
Et	Br	H	H	4.74	0.39	-0.57	0.44	291.00	66.31	11.01 ± 0.23
Et	Br	Br	Br	5.50	0.44	-0.52	0.40	430.80	93.80	13.48 ± 0.17
Et	I	H	H	3.78	0.34	-0.60	0.46	280.60	72.16	10.57 ± 0.27
Et	I	I	I	3.10	0.49	-0.58	0.44	383.00	132.60	11.54 ± 0.27
Et	N ₃	H	H	5.88	0.51	-0.31	0.24	320.00	80.89	11.31 ± 0.07
Me	CHO	H	H	12.30	0.52	-0.34	0.26	534.50	70.20	15.85 ± 0.17
Et	Ac	H	H	9.14	0.48	-0.30	0.23	467.50	80.63	14.44 ± 0.10
Et	Ac	Ac	Ac	9.97	0.41	-0.30	0.23	594.80	91.43	16.51 ± 0.10
Me	CN	H	H	18.03	0.44	-0.34	0.26	748.50	65.87	19.25 ± 0.13
n-Hex	NO ₂	H	H	14.90	0.37	-0.30	0.23	906.70	94.60	20.98 ± 0.07
n-Hex	NO ₂	NO ₂	NO ₂	19.80	0.43	-0.45	0.35	1383.00	138.30	26.02 ± 0.30

3-Cyano-9-methylcarbazole

3-Formyl-9-methylcarbazole oxime (22.43 g; 0.01 mol) and anhydrous sodium acetate (2.0 g) in 150 cm³ of acetic anhydride were refluxed for 6 h. The anhydride was distilled off in vacuum and the residue crystallized from ethanol yielding 18.45 g of the crude product, m.p. = 93–95°C. It was dissolved in methylene chloride, the solution was diluted with hexane, boiled with charcoal and filtered. A cooled solution deposited 16.50 g (80 %) of 3-cyano-9-methylcarbazole; colourless needles, m.p. = 95–96°C.

For C₁₄H₁₀N₂ (*M_r* = 206.24) *w_i*(calc.): 81.53 % C, 4.89 % H; *w_i*(found): 81.60 % C, 4.98 % H.

Mass spectrometry, *m/z*(*I_r*): 207(15.2), 206(*M*⁺, 100.0), 205(41.3), 191(6.5), 178(3.0), 177(6.5), 165(4.3), 164(5.2), 152(2.8), 151(7.4), 140(2.0), 102(9.1). IR spectrum (KBr), $\tilde{\nu}/\text{cm}^{-1}$: 730, 755, 805, 890 (out of plane hydrogen wagging, 3-substituted carbazole system); 1250, 1330, 1470, 1590 (skeletal vibrations); 2210, 2220 (C—N stretching vibrations); 1360, 2830, 2950 (deformations and stretchings of the N—Me group); 3060 (aromatic C—H stretch).

All the compounds gave satisfactory elemental analyses. Before measurements the samples were recrystallized from either benzene, toluene, hexane or mixture thereof to avoid their contamination with polar solvents.

Table 2

Dipole moments of 3,6-disubstituted 9-alkylcarbazoles

9-Alkyl	3,6-Substituents	$\mu_{\text{exp}}/(10^{-30} \text{ Cm})$	$\mu_{\text{R}}/(10^{-30} \text{ Cm})$	$\mu_{\text{int}}/(10^{-30} \text{ Cm})$
Me	NMe ₂	3.34 ± 0.50	−3.24	−9.04
n-Hexyl	NH ₂	5.70 ± 0.20	+0.83	−4.97
Me	Me	4.50 ± 0.17	6.27	+0.47
Et	H	5.80 ± 0.13	5.80	0
Et	I	11.54 ± 0.27	4.80	−1.00
Et	Br	13.48 ± 0.17	5.94	+0.14
Et	Cl	13.18 ± 0.10	5.54	−0.26
Et	Ac	16.51 ± 0.10	7.00	+1.20
n-Hexyl	NO ₂	26.02 ± 0.30	6.84	+1.04

Results

The dipole moments of 3,6-disubstituted 9-alkylcarbazoles are collected in Table 2. To demonstrate the interaction between the substituent and carbazole system we have assumed that:

- a) a dipole moment of a derivative is parallel to the two-fold symmetry axis as in carbazole itself;

Table 3

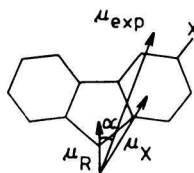
Dipole moments of 3-substituted 9-alkylcarbazoles

9-Alkyl	3-Substituent	$\mu_{\text{exp}}/(10^{-30} \text{ Cm})$	$\mu_{\text{R}}/(10^{-30} \text{ Cm})$	$\mu_{\text{int}}/(10^{-30} \text{ Cm})$	$\alpha/^\circ$	$\mu(\text{DMA})/(10^{-30} \text{ Cm})$
Me	NMe ₂	4.90 ± 0.37	-0.47	-6.27	223	3.60
Et	NH ₂	6.07 ± 0.03	-3.17	-8.94	205	4.44
Me	Me	5.10 ± 0.10	+5.90	+0.10	347	4.37
Et	I	10.57 ± 0.27	6.70	0.90	18	11.54
Et	Br	11.01 ± 0.23	6.60	0.80	20	11.24
Et	Cl	10.43 ± 0.10	6.34	0.53	23	10.97
Et	N ₃	11.31 ± 0.07	7.34	1.53	17	—
Et	Ac	14.44 ± 0.10	8.97	3.17	24	16.85
Me	CHO	15.85 ± 0.17	10.21	4.40	16	18.68
Me	CN	19.25 ± 0.13	7.07	1.27	29	19.68
n-Hexyl	NO ₂	20.98 ± 0.07	9.11	3.30	32	23.12

- b) it is a vector sum of the dipole moment of the skeleton (μ_R) and those of substituents (μ_X); possible conformers are populated statistically;
- c) contributions of substituents X can be approximated with the dipole moments of the benzene derivatives PhX (from [14, 15]);
- d) the geometry of the carbazole system [16] remains intact in spite of the substituents present.

Now the dipole moment of the heteroaromatic skeleton (μ_R) can be simply calculated from the experimental value. In the last column of Table 2 interaction moments $\mu_{int} = \mu_R - 5.80 \times 10^{-30}$ Cm are listed. These values can be considered as the gauge of polarization of the π -electron system under influence of substituents.

In Table 3 where dipole moments of 3-substituted 9-alkylcarbazoles are listed, the symbols used have the same meaning, however the μ_R values were calculated in somewhat different manner (Scheme 2). It has been assumed that estimated values μ_{exp} are vector sums of the components as in Scheme 2, hence each value of the interaction moment is accompanied with the angle α between the symmetry axis of the carbazole system and direction of the dipole moment. In the last column the dipole moments of *para*-X-substituted *N,N*-dimethylanilines (DMA's) are given (data from the tables [14, 15]).



Scheme 2

The influence of the length of an alkyl chain on the dipole moments is negligible, *e.g.* 3-amino-9-ethyl- and 3-amino-9-n-hexylcarbazole have the same $\mu_{exp} = (6.07 \pm 0.13) \times 10^{-30}$ Cm. Analogously the difference between the dipole moment of 3,6-diiodo-9-ethylcarbazole $((11.54 \pm 0.27) \times 10^{-30}$ Cm) and 3,6-diiodo-9-benzylcarbazole $((11.51 \pm 0.27) \times 10^{-30}$ Cm) is within the experimental error.

Discussion

Interaction moments of 3,6-disubstituted 9-alkylcarbazoles reflect the contribution of the mesomeric structures with separated charges to the resonance hybrid. Electron-withdrawing substituents increase slightly the dipole moments

DIPOLE MOMENTS

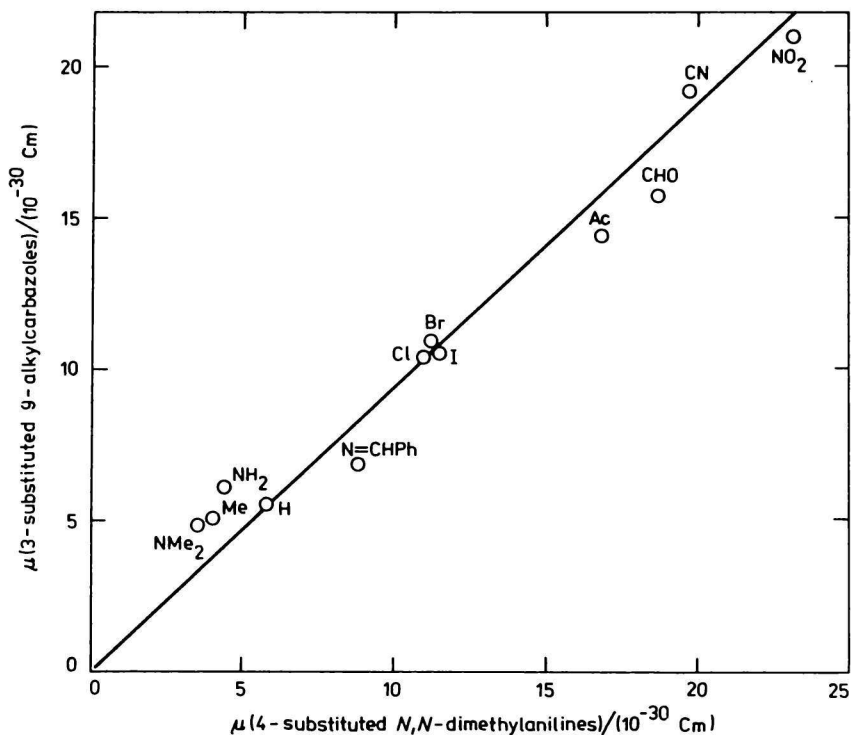


Fig. 1. Comparison of the dipole moments of 3-substituted 9-alkylcarbazoles and 4-substituted *N,N*-dimethylanilines.

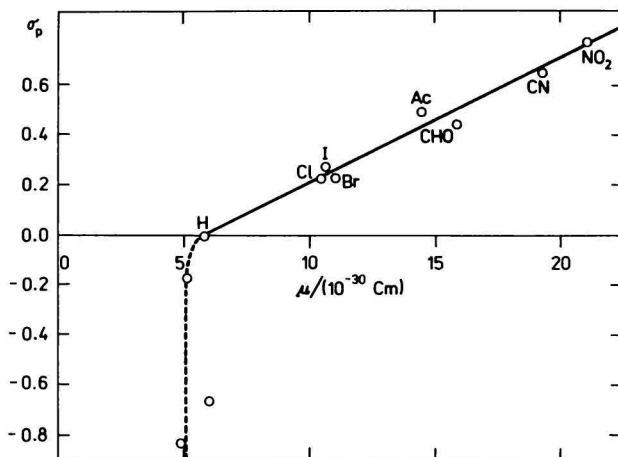


Fig. 2. Relationship between the dipole moments of 3-substituted 9-alkylcarbazoles and the σ_p constants of the substituents.

of the aromatic system (*ca.* 1.33×10^{-30} Cm). Negative values of interaction moments of the amino derivatives indicate that strongly donating substituents decrease conjugation between pyrrole nitrogen and carbocyclic rings. In the 3,6-bis(*N,N*-dimethylamino)-9-methylcarbazole molecule the dipole moment of the skeleton has the opposite direction as compared with unsubstituted 9-ethylcarbazole. There is however no correlation between the interaction moments and donor-acceptor properties of substituents expressed as the σ constants.

Within the mono substituted series the interaction moments are significantly greater. This effect can be rationalized as the result of the diversified direction of dipole moments. In 3-nitro-9-n-hexylcarbazole the vector is nearly parallel to the N—C-9a—C-3—NO₂ axis while in 3-(*N,N*-dimethylamino)-9-methylcarbazole it has the opposite direction. Again delocalization of the pyrrole nitrogen lone pair (or its absence) determines the dipole moments of carbazole derivatives. In fact, the direction of dipole moments is hypothetical because the reasoning reported above is only one of the possible interpretations but there are some relationships which support this point of view.

If the dipole moments of naphthalene derivatives [17] are plotted against those of substituted benzenes the straight lines are obtained with the slopes equal to unit for 1-substituted naphthalenes and slightly higher (1.05×10^{-30} Cm) for the 2-isomers. There is a similar relationship between the dipole moments of 3-substituted carbazoles and 4-substituted *N,N*-dimethylanilines (Fig. 1). It seems that the polarizability of the both aromatic systems is similar, *i.e.* the interaction of a substituent with either pyrrole or amino nitrogen is of the same kind and the unsubstituted ring of the carbazole system does not contribute to the dipole moment of the molecule.

It has been pointed out by Exner [18] that there can be no general relationship between the σ constant and dipole moment because the former reflects the influence of a substituent on a particular site of the molecule (*i.e.* the reacting bond) while the latter is the property of a molecule as a whole. Dipole moments of 3-substituted 9-alkylcarbazoles when plotted against σ_p constants give the straight line with the $\sigma_p > 0$ region, *i.e.* for the electron-withdrawing substituents (Fig. 2). Dipole moments of derivatives containing donor substituents vary within a narrow range ($(4.90\text{--}6.07) \times 10^{-30}$ Cm) and do not correlate with the σ_p constants.

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