Fluorene Derivatives with Intramolecular Charge-transfer: Exceptionally Easy Rotation Around the Double C(9)=C(α) Bond in Nitro-substituted 9-Aminomethylenefluorenes

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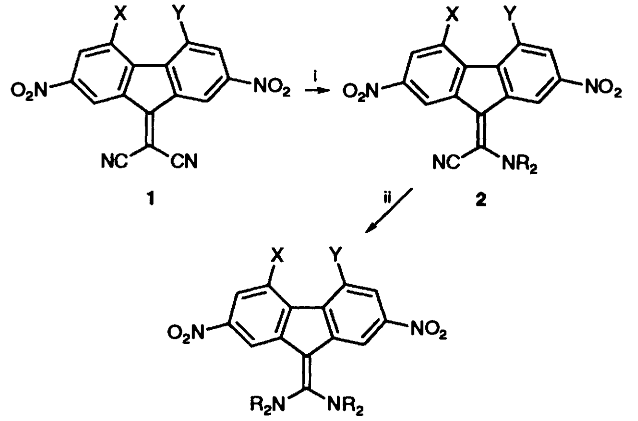
Strong intramolecular charge-transfer which occurs in fluorenes **2** and **3** from the donor amino group(s) to the acceptor fluorene moiety leading to exceptionally easy rotation around the C(9)=C(α) bond has been observed in solution by ^1H NMR and UV–VIS spectroscopy; single crystal X-ray analysis of compound **2h** shows significant π-bond delocalization along the C(9)–C(14)–N(2) fragment.

Electron acceptors of the fluorene series are gaining attention in the study of intermolecular charge-transfer complexes which possess specific electro-physical properties, as electron transport materials and as photoconductivity sensitizers for carbazole-containing polymers.[1] Recently, it has been shown[2] that photoconductive polymers containing electron acceptors of the fluorene series with intramolecular charge-transfer (ICT) may exhibit increased photoconductivity in the ICT region. Therefore, a study of the influence of the structure of fluorene compounds containing both acceptor and donor moieties upon ICT energies is of considerable interest.

Strong electron acceptors having a dicyanomethylene fragment, *e.g.* TCNQ (E_A = 2.88 eV) and TCNE (E_A = 2.75 eV)[3] react with aliphatic amines by substitution of one or two cyano groups by amino groups.[4] It is known that similar cyano-group substitution occurs for the strongest electron acceptor of the fluorene series, *i.e.* 9-dicyanomethylene-2,4,5,7-tetranitrofluorene (**1h**, E_A = 2.6 eV).[5] We now report that nitro-derivatives of 9-dicyanomethylenefluorene (**1a–g**) with lower electron affinity values, react with secondary amines with subsequent substitution of cyano groups by amino groups, similar to acceptor **1h**, although in lower yields† (Scheme 1). The presence of the electron donating substituent (R_2N) and the acceptor fluorene fragment in molecules **2** and **3**‡ results in ICT which is manifested in the appearance of an additional band in the visible region (*i.e.* the ICT-band) in the electronic absorption spectra. For derivatives with an unsymmetrical fluorene fragment (*i.e.* different substituents X and Y) for compound **2** (and for compounds **3** with different amine substituents) two isomers (*i.e.* *Z* and *E*) about the C(9)=C(α)§ bond may exist.

Accordingly, ^1H NMR spectra of these compounds have been studied. The spectrum for compound **2c** in acetone solution shows that it exists with *Z*:*E* isomer ratio close to 50:50. However, the energy of the *Z*–*E* transition is unusually low, so that when the sample is heated and/or a more polar solvent, *e.g.* DMSO, is used, one observes broadening and coalescence of the proton signals of the fluorene ring corresponding to the *Z* and *E* isomers due to increased rate of rotation around the formally double C(9)=C(α) bond. Increasing the number of electron-withdrawing substituents on the ring system also results in a lowering of the rotation barrier. Thus, for compound **2h** in acetone (18 °C) sharp doublet (δ 8.70, $J_{1,3}$ 2.0 Hz) and broad singlet (δ 9.11) peaks for protons 3,6-H and 1,8-H, respectively, are observed due to fast rotation (on the NMR time-scale). Cooling a sample of **2h** results in decoalescence of the 1,8-H protons and in coalescence of the 3,6-H protons, and at −90 °C two sharp doublets (δ 9.50, 8.71) for 1- and 8-H and a singlet (δ 8.68) for 3,6-H are observed. A rotation deceleration may also be achieved by increasing the steric hindrance in the amine: thus, for compound **2f** in acetone (20 °C) for R = CH_3 broadened proton signals 1,3,6,8-H are observed, whereas for R_2N = $C_5H_{10}N$–, $CH_2CH_2OCH_2CH_2N$– the ^1H NMR spectrum displays sharp signals from the separate *Z* and *E* isomers.



a X = Y = H
b X = C(O)NMe$_2$; Y = H
c X = CO_2Me; Y = H
d X = $CO_2C_4H_9$; Y = H
e X = CN; Y = H
f X = NO_2; Y = H
g X = CO_2Me; Y = NO_2
h X = Y = NO_2

Scheme 1 *Reagents and conditions:* (i) R_2NH (1.05–1.1 equiv.), dioxane, 25 °C, 20 min–6 h (monitored by TLC); (ii) R_2NH (4–6 equiv.), acetonitrile, 25–80 °C, 40 min–2 days (monitored by TLC)

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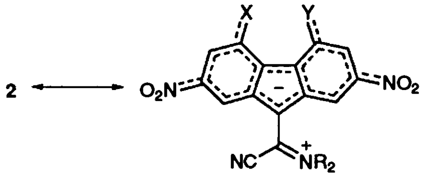
† The reaction is complicated by side processes of nucleophilic attack by other reaction sites, *i.e.* nitro-group substitution, C(9) carbon attack resulting in fluorenones, *etc.*

‡ Satisfactory elemental analysis; UV-VIS and ^1H NMR spectra were obtained for all new compounds; mp/°C for R = CH_3: 299–300 (**2a**), 287–288 (**2b**), 246.5–247.5 (**2c**), 163–164 (**2d**), 300–302 (**2e**), 270–273 (**2f**), 249–252 (**2g**), 296–298 (**2h**), 227–230 (**3a**), 258–262 (**3b**), 260–261 (**3c**), 183–184 (**3d**), 322–324 (**3e**), 294–296 (**3f**), 278–280 (**3g**), > 360 (**3h**); for R_2N = piperidino: 304.5–306.5 (**2f**); for R_2N = morpholino: 244–246 (**2f**), > 360 (**3f**).

§ In the crystallographic diagram (Fig. 1) C(α) is numbered as C(14).

With compounds **3a–f** the rotation barrier around C(9)=C(α) bond is lowered still further and time-averaged signals of *Z* and *E* isomers are observed at both −90 and +18 °C. Moreover, rotation around the C(α)–NR_2 bond becomes hindered resulting in magnetic inequivalence of the substituents R at one nitrogen atom; thus, for compounds **3** with R = CH_3, two singlets from the methyl groups are observed [with R=R′ the *Z–E* transition is degenerate. Experiments using amines with different groups R and R′ (dimethylamine and morpholine) confirm the correct assignment of the signals].

This remarkably easy rotation around a C=C double bond in solution is accounted for by the pronounced dipolar nature of compounds **2** and **3** resulting from intramolecular charge-transfer represented by resonance structures **4** and **5**, respectively.



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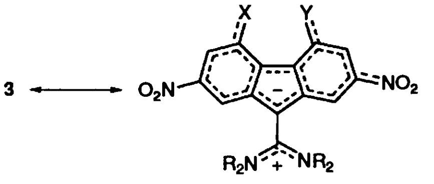

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To study this ICT process in the solid state the molecular structure of compound **2h**, was determined by single crystal X-ray analysis (Fig. 1).* Indeed, the exocyclic double bond C(9)=C(14) is conjugated with the lone electron pair of N(2), resulting in significant π-bond delocalization along the C(9)–C(14)–N(2) moiety. The bond distances C(9)–C(14) 1.388(4) and C(14)–N(2) 1.342(4) Å correspond to bond numbers of 1.55 and 1.40, respectively.[6] The slight twist around these bonds (by 19° and 25°, respectively) and the non-planarity of the bond configuration around N(2) [which deviates from the C(14)C(16)C(17) plane by 0.13 Å, the sum of the C–N–C angles being 357.4°] are both consistent with such a description. Similar structural behaviour (change of bonds lengths, near planar sp^2 configuration of the nitrogen atoms of amino-groups) has been observed recently for other compounds of the push–pull type, *e.g.* 1,1-dicyano-2,2-bis(dimethylamino)ethylene,[7] its cumulogues and vinylogues.[8] The molecule **2h** exhibits minor but significant non-planarity. Mean planes of the six-membered rings A and C form a dihedral angle of 12°. This puckering is apparently caused by steric hindrances between the adjacent nitro-groups (in positions 4 and 5), which are tilted out of the ring planes in the opposite directions [N(4) and N(5) deviating from these planes by 0.30 and −0.33 Å] and rotated around the C–N bonds, thus forming dihedral angles of 34° and 40° with the rings A and C, respectively. These results are consistent with nitro-group rotation by 27° to 42° in other 4,5-dinitro-substituted fluorenes.[9]

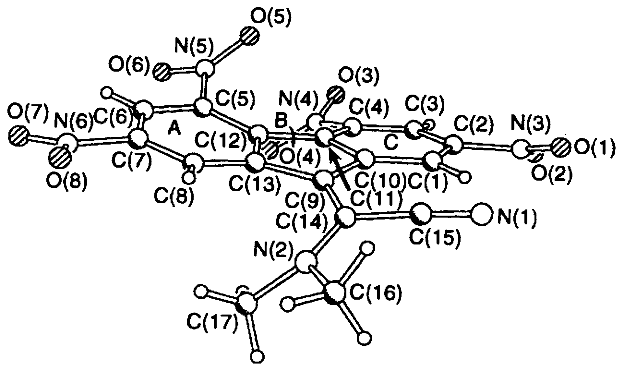

Fig. 1 X-Ray molecular structure of compound **2h**; selected bond lengths and angles (Å, °): N(1)–C(15) 1.145(4), N(2)–C(14) 1.342(4), N(2)–C(16), 1.478(5), N(2)–C(17) 1.456(4), C(9)–C(10) 1.464(4), C(9)–C(13) 1.455(4), C(9)–C(14) 1.388(4), C(11)–C(12) 1.459(4), C(14)–C(15) 1.460(4), N(4)···O(5) 2.66, N(5)···O(4) 2.64, O(4)···O(5) 2.83; N(1)–C(15)–C(14) 177.2(3), C(15)–C(14)–C(9) 118.5(2), N(2)–C(14)–C(9) 127.9(2), C(14)–N(2)–C(16) 121.1(2), C(14)–N(2)–C(17) 123.1(3), C(16)–N(2)–C(17) 113.2(2), C(14)–C(9)–C(10) 126.2(2), C(14)–C(9)–C(13) 127.7(3), C(10)–C(9)–C(13) 105.9(2), N(5)–C(5)–C(6) 115.5(3), N(5)–C(5)–C(12) 122.5(3)

Intramolecular donor–acceptor interaction in compounds **2** and **3** is also manifested in their electron absorption spectra: in the visible region additional absorption bands corresponding to ICT transitions appear.† Compounds **3** show a bathochromic shift of the ICT band compared with analogues **2** (for **2** $\lambda_{ICT} \approx$ 440–550 nm, for **3** λ_{ICT} = 530–620 nm) and a decrease in its intensity. This is in contrast to TCNQ and TCNE derivatives where substitution of the second cyano-group is accompanied by a hypsochromic shift of the ICT band.[4]

A bathochromic shift of the ICT band is also observed when the number of electron-withdrawing substituents in compounds **2** and **3** increases. Quantitative estimation of the effect of substituents in the fluorene ring of compounds **2** and **3** upon the energies of ICT bands was carried out by eqn. (1) where $\Sigma\sigma_p^-$

$$h\nu_{ICT}/h\nu^0_{ICT} = \rho^-\Sigma\sigma_p^- \quad (1)$$

is a sum of σ_p^- nucleophilic constants of the substituents in the fluorene nucleus (X, Y and two nitro-groups), $h\nu_{ICT}$ is the ICT energy defined by the maximum of the ICT bands (λ_{ICT}), and ρ^- is a parameter showing ICT energy sensitivity to substituents.

The data on the influence of substituents in various solvents are given in Table 1 indicating good correlation in all the cases. Sensitivity of ICT energies to the influence of substituents, ρ^-, decreases when passing from compounds **2** to compounds **3**. For both series of compounds a tendency to ρ^- growth with increasing solvent polarity is observed which is indicative of higher polarity of the excited state in compounds **2** and **3** as compared to the ground state.‡ Attempts at quantitative estimation of the solvent influence upon ICT energies using the Koppel–Palm four-parameters' equation[10] which separately considers polarity $(\varepsilon - 1/2\varepsilon + 1)$, polarizability $(n^2 - 1/n^2 + 1)$, basicity (*B*) and acidity (*E*) of the solvent show that

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* *Crystal data* for **2h**: $C_{17}H_{10}N_6O_8$, *M* = 426.3, monoclinic space group *C2/c*,*a* = 19.313(6), *b* = 10.680(3), *c* = 17.036(5) Å, β = 98.48(3)°, *U* = 3475(2) $Å^3$, *Z* = 8, D_c = 1.63 g cm^{-3}, *F*(000) = 1744, Mo-K_α radiation, λ = 0.7103 Å. *T* = 150 K. The structure was solved by direct methods and refined by full-matrix least-squares against *F*s of 2196 reflections having $F \geq 4\sigma(F)$ and $2\theta \leqslant 54°$, with $w = [\sigma^2(F) + 0.0002F^2]^{-1}$ weights using SHELXTL PLUS software. All non-hydrogen atoms were refined with anisotropic displacement parameters and all H atoms in isotropic approximation (total of 322 variables), converging at *R* = 0.047, R_w = 0.048 and goodness-of-fit 1.33, $\Delta\rho_{max}$ = 0.26 e $Å^{-3}$, max. shift/esd ratio 0.004. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, see 'Instructions to Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

† The intramolecular nature of this transition is corroborated by studies of concentration dependences of CT band intensities.

‡ Plots of ρ^- *vs.* $\varepsilon^{0.5}$ display curvilinear dependence (increasing ρ^- with increase of $\varepsilon^{0.5}$) for **2** and bell-like dependence with ρ^-_{max} at $\varepsilon \approx 25$ for **3** (from data of Table 1).

Table 1 Parameters ρ^- of the ICT energies' sensitivity to substituents in the fluorene ring in compounds **2** and **3** in various solvents, 25 °C

			2a, c–h		**3a, c, d, f–h**	
Solvent	ε[a]	B[b]	$\rho^- \times 10^2$	r[c]	$\rho^- \times 10^2$	r[c]
Dioxane	2.209	237	-14.0 ± 0.6	-0.996	-6.9 ± 0.5	-0.990
Benzene	2.284	48	-13.2 ± 0.5	-0.997	-5.8 ± 0.6	-0.982
Chlorobenzene	5.62	38	-14.9 ± 0.8	-0.993	-6.8 ± 0.5	-0.990
AcOH	6.15	139	-15.6 ± 1.0	-0.990	-8.2 ± 0.7	-0.987
o-Dichlorobenzene	9.93		-14.9 ± 0.3	-0.999	-7.3 ± 0.4	-0.995
Acetone	20.74	224	-17.4 ± 0.9	-0.993	-8.5 ± 0.4	-0.996
Dimethylformamide	36.7	291	-17.6 ± 1.0	-0.992	-7.9 ± 0.4	-0.996
Acetonitrile	37.5	160	-17.5 ± 0.8	-0.995	-8.4 ± 0.3	-0.997
Dimethyl sulfoxide	48.9	362	-18.0 ± 1.2	-0.990	-7.4 ± 0.2	-0.998

[a] Relative permittivity. [b] Basicity of the solvent (see ref. 10). [c] Correlation coefficient.

in all cases it is only polarity and basicity that prove to be statistically relevant.*

In summary we have synthesized a series of novel nitro-substituted 9-aminomethylenefluorene acceptors **2** and **3** and established that intramolecular charge-transfer occurs in solution leading to exceptionally easy bond rotation about the C(9)=C(α) bond. Consistent with this, the single crystal X-ray structure of **2h** shows significant bond delocalization along the C(9)–C(14)–N(2) fragment.

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* Correlation coefficients $R = 0.95$–0.99 for **3** and $R = 0.90$–0.96 for **2** have been obtained.

References

1 M. Matsui, K. Fukuyasu, K. Shibata and H. Muramatsu, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1107; H. Hoegl, G. Barchietto and D. Tar, *Photochem. Photobiol.*, 1972, **16**, 335.

2 N. G. Kuvshinsky, N. G. Nakhodkin, N. A. Davidenko, A. M. Belonozhko and D. D. Mysyk, *Ukr. Fiz. Zh.*, 1989, **34**, 1100 (*Phys. Abstr.*, 1989, **92**, 142486); N. M. Semenenko, V. N. Abramov, N. V. Kravchenko, V. S. Trushina, P. G. Buyanovskaya, V. L. Kashina and I. V. Mashkevich, *Zh. Obsch. Khim.*, 1985, **55**, 324 (*Chem. Abstr.*, 1985, **103**, 53782h).

3 V. E. Kampars and O. Ya. Neilands, *Usp. Khim.*, 1977, **46**, 945 (*Chem. Abstr.*, 1977, **87**, 101429y); J. B. Torrance, *Mol. Cryst. Liq. Cryst.*, 1985, **126**, 55.

4 W. R. Hertler, H. D. Hartzler, D. S. Acker and R. E. Benson, *J. Am. Chem. Soc.*, 1962, **84**, 3387; B. C. McKusick, R. E. Heckert, T. L. Cairus, D. D. Coffman and H. F. Mower, *J. Am. Chem. Soc.*, 1958, **80**, 2806.

5 B. P. Bespalov and G. A. Tashbayev, *Zh. Org. Khim*, 1980, **16**, 843 (*Chem. Abstr.*, 1980, **93**, 114180j).

6 L. Pauling, *The Nature of the Chemical Bond*, Ithaca, Cornell Univ. Press, 1960, p. 232.

7 D. Adhikesavalu and K. Venkatesan, *Acta. Crystallogr., Sect. C*, 1983, **39**, 589.

8 B. Tinant, J.-P. Declerq, D. Bouvy, Z. Janousek and H. G. Viehe, *J. Chem. Soc., Perkin Trans. 2*, 1993, 911.

9 O. V. Semidetko, L. A. Chetkina, V. K. Bel'skii, A. N. Poplavskii, A. M. Andrievskii and K. M. Dyumaev, *Dokl. Akad. Nauk SSR*, 1988, **299**, 375 and refs. cited therein (*Chem. Abstr.*, 1989, **111**, 96782r); O. V. Semidetko, L. A. Chetkina, V. K. Bel'skii, A. N. Poplavskii, A. M. Andrievskii and K. M. Dyumaev, *Zh. Strukt. Khim.*, 1988, **29**, 187 (*Chem. Abstr.*, 1988, **109**, 139617u); R. G. Baughman, *Acta Crystallogr., Sect. C*, 1987, **43**, 933.

10 I. A. Koppel and V. A. Palm, in *Advances in Linear Free Energy Relationships*, ed. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, ch. 5, p. 203.

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