Letter

Twisted intramolecular charge transfer fluorescence in nitro-substituted α,ω-diphenylpolyene compounds

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A fluorescence study of 1-*p*-cyanophenyl-4-phenylbuta-1*E*,3*E*-diene (2), 1-*p*-nitrophenyl-4-phenylbuta-1*E*,3*E*-diene (3), and 1-*p*-nitrophenyl-4-*p*-cyanophenylbuta-1*E*,3*E*-diene (4) in solvents of varying polarity at ambient temperature and in a 1 : 1 ethanol–methanol matrix at 298 and 77 K revealed that the nitro-substituted compounds are capable of exhibiting unusually red-shifted fluorescence emissions due to a twisted intramolecular charge transfer excited state.

The photoprocesses of α,ω-diphenylpolyenes[1] [C_6H_5-$(CH{=}CH)_nC_6H_5$] have attracted a great deal of attention[2] because of their relevance to linear retinylidene polyenes that are related to sensory and bio-energy transductions[3] and because of their possible uses in all-optical ultra-fast switching applications[4] and probes for environmental polarity.[5] Upon absorption of photons, linear C=C chromophores produce a planar excited state which undergoes further twisting to yield the "perpendicular species" from which the *cis-trans* isomerization products are obtained.[2] Furthermore, fluorescence from the S_1 excited state effectively competes with the activated twisting of the C=C into the perpendicular geometry.[2] It has also been proposed that the development of charge as a function of twist angle in alkenes containing carbons of different electronegativities can cause a rapid increase in dipole moment as the perpendicular geometry is reached and dipolar zwitterionic species may be involved in the photoprocesses of such chromophores.[2,6] Photophysical studies of substituted diphenylbutadienes have suggested that in addition to locally excited states lower energy conformationally relaxed intramolecular charge transfer excited states can also be involved in the photoprocesses of linear polyenes.[7] However, the exact nature of the excited states of linear polyenes is not clearly understood. Additionally, fluorescent sensors and chromogenic indicators are of much current interest; however, only a few sensing systems and mechanisms have been described.[8] In this regard, the fluorescence from charge transfer excited states appears interesting because the intensity and peak position of such emissions can be greatly affected by solvent polarity and the fluorophores capable of exhibiting such emissions can find applications as environmental polarity probes and in optical ultra-fast switching mechanisms.

Donor–acceptor substituted α,ω-diphenylpolyenes represent interesting models for charge transfer studies in the excited state and hence we have designed 1,4-diarylbutadienes **2**–**4** [1-*p*-cyanophenyl-4-phenylbuta-1*E*,3*E*-diene, *p*-NCC_6H_4-$CH{=}CHCH{=}CHC_6H_5$, **2**; 1-*p*-nitrophenyl-4-phenylbuta-1*E*,3*E*-diene, *p*-$O_2NC_6H_4CH{=}CHCH{=}CHC_6H_5$, **3**; 1-*p*-nitrophenyl-4-*p*-cyanophenylbuta-1*E*,3*E*-diene, *p*-$O_2NC_6H_4CH{=}CHCH{=}CHC_6H_4CN$-*p*, **4**] and investigated their absorption, fluorescence emission and excitation properties along with the parent 1,4-diphenylbuta-1*E*,3*E*-diene (**1**, $C_6H_5CH{=}CHCH{=}CHC_6H_5$) in organic solvents of varying polarity at room temperature and in a 1 : 1 ethanol–methanol matrix at 298 and 77 K. We now report that diarylbutadienes having at least one nitro substituent on one of their phenyl rings as an acceptor group are capable of exhibiting unusually red-shifted fluorescence emissions due to a twisted intramolecular charge transfer (TICT) excited state.

The dienes were synthesized from their respective aldehydes and phosphonates by a generalized Emmons–Horner process.[9] All the dienes showed satisfactory physico-chemical data (UV-vis, IR, NMR, C,H,N elemental analysis) corresponding to their constitution and structure. The absorption and fluorescence data of compounds **1**–**4** in different solvents are summarized in Tables 1 and 2 and the corresponding fluorescence spectra are shown in Fig. 1 and 2. While the absorption λ_{max} of the parent diphenylbutadiene (**1**) is insensitive to solvent polarity, substituted dienes **2**–**4** exhibit a rather moderate red shift of 5–21 nm depending on the substituent and the solvent. As compared to **1**, cyano substituted diene **2** does not show much shift in its absorption λ_{max}. However, nitro substituted dienes **3** and **4** exhibit a substantial red shift in their absorption λ_{max} as compared to **1**.

In contrast to a rather moderate effect on the absorption spectra, solvent polarity markedly affects the fluorescence properties of **2**–**4**, particularly nitro-substituted dienes **3** and **4**. Thus, the magnitude of the red shifts in the fluorescence λ_{max} are much greater than those of the absorption λ_{max}. Diene **3** which has only a nitro substituent shows a more red-shifted fluorescence emission as compared to diene **4** which has both nitro and cyano substituents. However, the effect of solvent polarity on fluorescence λ_{max} is much greater in diene **4** than in diene **3**. Thus, the differences in fluorescence λ_{max} of **3** and **4** in non-polar *n*-heptane and protic-polar methanol are 136 and 188 nm, respectively. Thus, the cyano substituent has a destabilizing effect and solvent polarity has a stabilizing influence on the fluorescent species in the case of diene **4**.

The corresponding Stokes' shifts in **3** and **4** are found to be relatively large and increase with solvent polarity. The Lippert–Mataga plots[10] [Stokes' shift *vs.* solvent parameter, Δf] showed large changes in the excited state dipole moments ($\Delta\mu$) of **3** and **4** (20.9 and 19.7 Debye respectively). The fluorescence λ_{max} is not affected by increasing the concentrations of dienes in the 1.0×10^{-3}–1.0×10^{-5} M range. The presence of cyano and nitro substituents on the aromatic rings causes a drastic decrease in the fluoresce quantum yield (Φ_f) as compared to unsubstituted parent diene **1** (Table 1). The nitro substituted dienes are particularly found to have very low Φ_f, except in acetonitrile and DMF.

The dependence of the Stokes' shift ($\nu_a - \nu_f$) on the solvent polarity has also been correlated with solvent parameters [$E_T(30)$][11] and '*R*'.[12] When the empirical Dimroth parameter [$E_T(30)$], used as a measure for the solvent polarity, was increased, ($\nu_a - \nu_f$) increases almost linearly for the nitro substituted dienes **3** and **4** and the slope is markedly larger for these dienes in comparison to cyano-substituted diene **2** which

Table 1 Photophysical and solvent polarity parameter R values of dienes **2**–**4** at 298 K

Diene[a]	Solvent[b]	λ_{max}/nm Abs	Em[c]	Ex[d]	Φ_f [e]	Stokes' shift/ cm^{-1}	R
2	*n*-Heptane	344	406	344	0.003	4439	−0.0949
	Dioxane	347	407	345	0.007	4248	−0.1646
	THF	346	418	346	0.007	4978	−0.0133[g]
	DMF	349	422	345	0.014	4956	0.0501
	MeCN	344	421	343	0.003	5260	0.0229
	Dioxane–40% H_2O	346	421	344	0.007	5210	−0.0620
	MeOH	344	421	343	0.004	5260	−0.0476
	Dioxane–70% H_2O	344	423	344	0.010	5480	−0.0756
3	*n*-Heptane	370	470	334	0.002	6000	−0.8394
	Dioxane	375	495	389	0.006	6464	−1.2184
	THF	374	508	383	0.003	6875	−1.0330[g]
	DMF	383	567	386	0.295	9000	−0.4477
	MeCN	378	574	377	0.174	8998	−0.4860
	Dioxane–40% H_2O	378	607	397	0.012	9520	−0.1074
	MeOH	379	606	378	0.003	9848	−0.0981
	Dioxane–70% H_2O	380	630	398	0.007	10440	−0.3555
4	*n*-Heptane	362	400	343	0.001	2620	−1.2833
	Dioxane	368	463	351	0.001	5575	−1.3268
	THF	378	485	384	0.001	6190	−1.0130[g]
	DMF	381	540	385	0.148	7730	−0.3220
	MeCN	374	539	376	0.078	8400	−0.6070
	Dioxane–40% H_2O	378	564	387	0.012	9174	−0.0918
	MeOH	375	588	377	0.003	9950	−0.0476
	Dioxane–70% H_2O	383	603	378	0.004	9800	−0.3980

[a] 1.0×10^{-5} M. [b] Solvents are in order of increasing $E_T(30)$ values taken from ref. 11. [c] At absorption λ_{max}. [d] At emission λ_{max}. [e] Relative to quinine sulfate standard ($\Phi_f = 0.515$)[14] at 298 K. [f] For determination of R, the values of S, which is a constant related to the polarity of solvent, are taken from ref. 12. [g] Determined taking S value equal to dioxane.[12] 1,4-Diphenylbuta-1*E*,3*E*-diene (**1**): Abs λ_{max}, 345 nm and Em λ_{max}, 375–378 nm (in *n*-heptane, dioxane, methanol and acetonitrile). Relative Φ_f: 0.222 (*n*-heptane), 0.052 (dioxane), 0.015 (methanol), 0.009 (acetonitrile).

is devoid of a nitro substituent (Fig. 3). The solvent parameter 'R' is a measure of the sensitivity of the system to change in solvent polarity and its values for dienes **1**–**4** are given in Table 1. The 'R' values are mostly negative and range between −1.33 and 0.05 for the substituted dienes. In general, an increase in the solvent polarity results in an increase in the value of 'R' too.

The marked effects of solvent polarity on λ_{max} and Φ_f of nitro-substituted dienes can be attributed to significantly polar nitro-twisted excited states. The fluorescence and other related photoprocesses of these dienes should be highly dependent upon the order of the first two excited singlet states, *i.e.* A_g and B_u,[2,3] and the degree to which they interact. The size and nature of the barrier to excited state rotations are expected to be influenced significantly by the substituent and the solvent. For diphenylbutadiene in EPA glass, the $2A_g - 1B_u$ energy difference has been found to be only ≈130 cm^{-1} and hence changes in molecular geometry or solvent orientation are expected to influence the relative ordering of the two lowest excited states which are separated only by a very small energy splitting.[2,13] A reversal of the $2A_g - 1B_u$ level ordering in diphenylbutadienes between isolated molecules and solution conditions is suggested to be caused by preferential stabilization of the $1B_u$ state in a polarizable medium. In a non-polar solvent like *n*-heptane very weak fluorescence may be the result of a $A_g^* \rightarrow A_g$ symmetry forbidden transition, while in a polar environment the states are inverted from A_g^{-*} to B_u^{+*} which gives rise to the allowed $B_u^* \rightarrow A_g$ transition which is responsible for the relative increase in Φ_f. Thus, the lowest excited singlet state of 1,4-diphenylbuta-1*E*,3*E*-dienes containing an electron-withdrawing acceptor group on the *para* position of the phenyl ring can be B_u in nature, which because of its ionic character is further stabilized in polar solvents. In such situations, twisted intramolecular charge transfer can occur in the excited states of diphenylbutadienes having strong donor–acceptor groups.

At 77 K, while dienes **1** and **2** do not exhibit significant shifts in their fluorescence λ_{max}, considerably blue-shifted fluorescence is observed for dienes **3** and **4** (Table 2). The fluorescence quantum yields for all the four dienes increase at lower temperature in the glassy matrix. In the fluid environment of a 1 : 1 methanol–ethanol mixture the dienes exhibit fluorescence at different wavelengths ranging from 375 to 600 nm depending on the substituents. However, in a rigid matrix the fluorescence emission from the dienes occurs at lower wavelength in a rather narrow range. Thus, there is a large blue shift in fluorescence λ_{max} and an increase in Φ_f in a glassy matrix as compared to values observed in homogeneous media. The

Table 2 Fluorescence data for dienes **1**–**4** at 298 and 77 K in a 1 : 1 ethanol–methanol matrix

	Fluorescence at 298 K			Fluorescence at 77 K		
Diene[a]	λem[b]/nm	λex[c]/nm	Φ_f [d]	λem[b]/nm	λex[c]/nm	Φ_f [d]
1	375	335	0.018	379	334	1.0
2	418	347	0.007	412	328	1.0
3	600	385	0.003	492	403	0.288
4	576	387	0.005	480	398	0.075

[a] 1.0×10^{-5} M. [b] At absorption λ_{max}. [c] At emission λ_{max}. [d] Relative to quinine sulfate standard ($\Phi_f = 0.515$)[14] at 298 K.

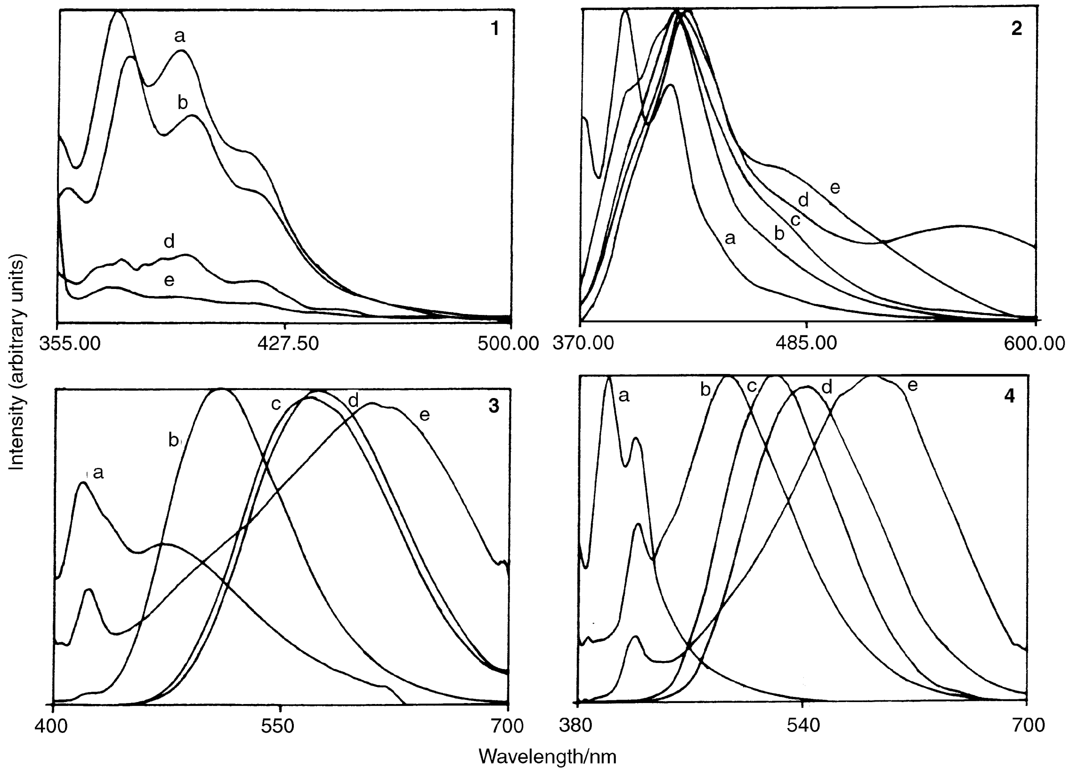

Fig. 1 Fluorescence spectra of **1**–**4** at 298 K in organic solvents of different polarity. (a) *n*-Heptane, (b) dioxane, (c) THF, (d) acetonitrile, (e) methanol. (In **3** and **4**, peaks near 420 nm are water Raman peaks.)

fluorescence spectra (emission and excitation) are also characterized by well-defined structures. In rigid media, molecular motion and solvent effects are absent resulting in a blue shift in emission λ_{max}, increase in Φ_f and well-defined structures in the emission and excitation spectra. There is no geometry change in the excited state of the molecule in a rigid matrix. The longer wavelength fluorescence of **3** and **4** at 298 K in a fluid environment may be due to the non-planar twisted intramolecular charge transfer excited states which are expected to be stabilized by a polar environment.

Owing to the different electronegativities present in the diene, intramolecular charge transfer in the excited state can occur *via* twisting of the bond between the nitro group relative to the attached phenyl (*i.e.* twisting about the C–N bond in $O_2N–C_6H_4$). Twisting of the C–C bond of the dienyl moiety between the rings is not likely as it will require a relatively larger volume of activation. Furthermore, large amplitude motion such as occurs at the beginning of a *cis-trans* isomerization is also unlikely as the time required for such motion would be too great for it to occur within a fluorescent lifetime.

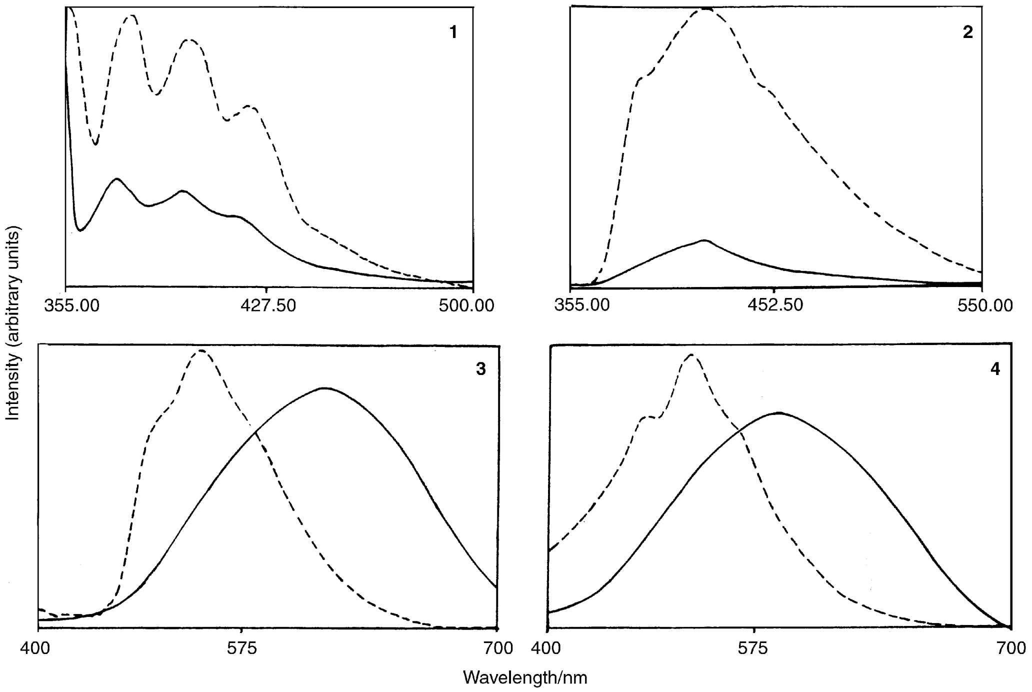

Fig. 2 Fluorescence spectra of **1**–**4** in ethanol-methanol (1 : 1) matrix at 298 K (——) and at 77 K (– – –).

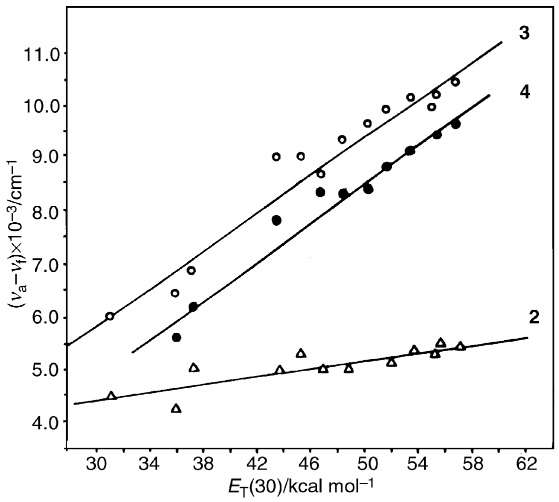

Fig. 3 A plot of solvent parameter $E_T(30)$ *vs.* Stokes' shift for dienes **2** (△), **3** (○), and **4** (●).

The $1B_u$ nature of the excited state can facilitate excited state twisted intramolecular charge transfer in dienes containing strong donor–acceptor groups. Given a small $2A_g - 1B_u$ splitting, small changes in molecular geometry or solvent orientation as the solvated molecule relaxes from its ground state configuration to an energy minimum on the excited state potential energy surface might account for the twisting of an appropriate bond as well as for some variations in fluorescence and related excited state properties.

Thus, appropriately substituted linear polyenes can involve polarized and twisted intramolecular charge transfer excited states in their photoprocesses. This study is also significant in retinylidene containing photoreceptor proteins and rhodopsins, and it further provides new directions for developing fluorescent sensor molecules and chromogenic indicators based on excited state twisted intramolecular charge transfer process.

Experimental

Physico-chemical data for dienes 2–4

1-*p*-Cyanophenyl-4-phenylbuta-1*E*,3*E*-diene 2. Yield 50%, mp 158–159 °C, UV-vis (THF): λ_{max}, 343 nm (ε, 54 000 l mol^{-1} cm^{-1}); IR, ν_{max} (cm^{-1}): 2900 (C–H str), 2250 (CN str), 1620, 1597 (C=C str), 978 (C–H def of *trans* alkene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.65 (1H, d, *J* = 15.01 Hz, $C_6H_5CH{=}CH$), 6.77 (1H, d, *J* = 14.65 Hz, *p*-NCC_6H_4-$CH{=}CH$), 6.96 (1H, dd, *J* = 14.83, 10.62 Hz, *p*-NCC_6H_4-$CH{=}CHCH{=}CH$), 7.05 (1H, dd, *J* = 14.83, 10.62 Hz, *p*-$NCC_6H_4CH{=}CHCH{=}$), 7.27–7.47 (5H, m, phenyl protons), 7.50 (2H, dd of AB quartet, *J* = 8.43, 1.83 Hz, *p*-NCC_6H_4), 7.60 (2H, dd of AB quartet, *J* = 8.42, 1.83 Hz, *p*-NCC_6H_4).

1-*p*-Nitrophenyl-4-phenylbuta-1*E*,3*E*-diene 3. Yield 60%, mp 166–168 °C, UV-vis (THF): λ_{max}, 375 nm (ε, 56 235 l mol^{-1} cm^{-1}); IR, ν_{max} (cm^{-1}): 2900 (C–H str), 1620, 1597 (C=C str), 1460 and 1386 (NO_2 str), 970 (C–H def of *trans* alkene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.70 (1H, d, *J* = 15.20 Hz, $C_6H_5CH{=}CH$), 6.80 (1H, d, *J* = 15.17 Hz, *p*-$NO_2C_6H_4$-$CH{=}CH$), 7.00 (1H, dd, *J* = 15.20, 10.44 Hz, $C_6H_5CH{=}CH$-$CH{=}$), 7.13 (1H, dd, *J* = 15.35, 10.44 Hz, *p*-$NO_2C_6H_4CH{=}CH$-$CH{=}$), 7.28–7.48 (5H, m, phenyl protons), 7.55 (2H, dd of AB quartet, *J* = 8.61, 2.38 Hz, *p*-$NO_2C_6H_4$), 8.20 (2H, dd of AB quartet, *J* = 8.61, 2.38 Hz, *p*-$NO_2C_6H_4$).

1-*p*-Cyanophenyl-4-*p*-nitrophenylbuta-1*E*,3*E*-diene 4. Yield 60%, mp 228–229 °C; UV-vis (THF): λ_{max}, 373 nm (ε, 50 000 l mol^{-1} cm^{-1}); IR ν_{max} (cm^{-1}): 2859 (C–H str), 2213 (CN str), 1578, (C=C str), 1569 and 1337 (NO_2 str), 1372 (C–N str of $C_6H_4NO_2$), 979 (C–H def of *trans* alkenes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.79 (1H, dd, *J* = 14.65, 10.25 Hz, *p*-$O_2NCC_6H_4CH{=}CH$), 6.93 (1H, dd, *J* = 14.65, 10.25 Hz, *p*-$NCC_6H_4CH{=}CHCH{=}$), 7.04 (1H, d, *J* = 14.83 Hz, *p*-$NCC_6H_4CH{=}$), 7.13 (1H, d, *J* = 14.83 Hz, *p*-$NO_2C_6H_4CH{=}CH$), 7.54 (2H, dd of AB quartet, *J* = 8.23, 1.64 Hz, *p*-NCC_6H_4), 7.64 (2H, dd of AB quartet, *J* = 8.42, 1.64 Hz, *p*-NCC_6H_4), 7.58 (2H, dd of AB quartet, *J* = 8.79, 1.83 Hz, *p*-$NO_2C_6H_4$); 8.21 (2H, dd of AB quartet, *J* = 8.79, 1.83 Hz, *p*-$NO_2C_6H_4$).

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Letter 9/07329I