

$R_3N^+N^-$: a substituent with extreme electronic effects

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Received 16 November 1999; revised 30 January 2000; accepted 4 February 2000

ABSTRACT: Basicity, infrared and x-ray results are reported which show the uniquely high electron-donor effect of $R_3N^+N^-$ substituents. An explanation is offered in terms of theoretically calculated resonance, field and electronegativity σ substituent constants. Large values of the calculated first-order hyperpolarizabilities in the $R_3N^+N^-(CH=CH)_nNO_2$ series suggest the introduction of the $R_3N^+N^-$ substituents in the synthesis of push–pull conjugated structures for second-order non-linear optics. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: basicity; infrared; substituent effects; push–pull molecules; hyperpolarizability

INTRODUCTION

The success of linear free energy relationships (LFER)¹ or quantitative structure–activity relationships (QSAR)² depends critically on the broadness of structural variation. For example, if substituent effects are investigated, sufficiently strong donor and acceptor groups should be present in the series. Such is the case with unipolar substituents (NH_3^+ , O^- , etc.) which affect reactivity rather strongly. However, attempts to determine their Hammett substituent constants¹ either gave different values according to the system used for definition, the solvent or the counterion,³ or require the introduction of special corrections.⁴ It is generally recommended^{5,6} not to include charged substituents with dipolar groups in data sets for LFER or QSAR. The common strongest electron donor group in many series appears to be the neutral substituent R_2N (dialkylamino).⁷ Indeed, many efficient push–pull systems, e.g. for non-linear optics⁸ or as solvatochromic probes,⁹ are of the kind R_2N-A or R_2N-T-A (A = acceptor and T = transmitter).

We studied here the electronic substituent effect of the dipolar ion, $R_3N^+N^-$, where cationic and anionic nitrogen are bonded together and carbon substituents are attached to the quaternary nitrogen ($H_3N^+N^-$ will also be used for calculations). We show the much more efficient electron-donating effect of the $R_3N^+N^-$ substituent rather than its R_2N counterpart, by comparing several chemical and physical properties of R_2N-A and $R_3N^+N^-A$ compounds, where A consists of various electron-withdrawing groups: COR , $C\equiv N$, NO_2 and SO_2R . In these push–pull molecules, the high basicity of

the carbonyl, cyano, nitro and sulfonyl groups, their low stretching vibration wavenumbers, and bond length and bond angle variations establish experimentally the extreme electron-donating properties of the $R_3N^+N^-$ substituent. This substituent effect is then described in terms of substituent constants σ from calculations, by standard computational methods, of three kinds of constants,^{10,11} σ_F , σ_R and σ_χ , corresponding to three assumed interaction mechanisms called field, resonance and electronegativity (the polarizability effect,^{10,11} relevant mainly for large alkyl groups in gas ion–molecule reactions, is not considered here). Finally, we calculate and compare the hyperpolarizability of the series of molecules $H_2N(CH=CH)_nNO_2$ and $H_3N^+N^-(CH=CH)_nNO_2$ in order to show the potential for non-linear optics brought about by introduction of the $R_3N^+N^-$ substituent in push–pull systems.

EXPERIMENTAL AND CALCULATIONS

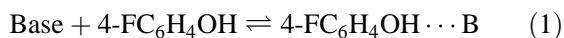
Materials. The synthesis of $R_3N^+N^-A$ compounds was described in previous papers.^{12–15}

Infrared measurements. The spectra were measured on Bruker IFS 48 Fourier transform infrared spectrometer (1 cm^{-1} resolution), as CCl_4 , $ClCH_2CH_2Cl$, or CH_2Cl_2 solutions, according to solubility and IR transparency.

Basicity data. The hydrogen-bond basicity, i.e. Lewis basicity towards hydrogen-bond donors, of the organic bases RA , R_2NA and $R_3N^+N^-A$, has been measured previously^{12–15} on the pK_{HB} scale¹⁶, which is defined by

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the equations



$$K_f (\text{dm}^3 \text{mol}^{-1}) = \frac{[4\text{-FC}_6\text{H}_4\text{OH} \cdots \text{B}]}{[\text{B}][4\text{-FC}_6\text{H}_4\text{OH}]} \quad (2)$$

$$\text{p}K_{\text{HB}} = \log K_f \quad (3)$$

Crystallographic data. Bond lengths and angles in R_2NA and $\text{R}_3\text{N}^+\text{N}^-\text{A}$ compounds were retrieved from the Cambridge Structural Database (CSD)¹⁷ (1999 release).

Computational details. All calculations were performed using Gaussian 94.¹⁸

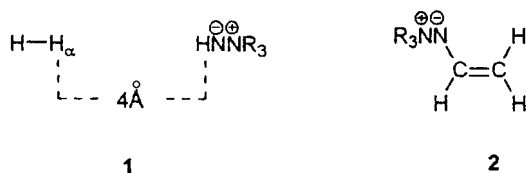
σ Calculations. For calculating σ_{F} , σ_{R} and σ_{χ} we closely followed the Topsom method,¹¹ recently validated by Exner *et al.*¹⁹ The field constant σ_{F} is calculated from the polarization of the H—H bond of an H_2 molecule by the $\text{HN}^-\text{N}^+\text{R}_3$ molecule held at 4 Å (**1**) by the equation

$$\sigma_{\text{F}} = -35.5 \Delta q_{\text{H}\alpha} \quad (4)$$

where $\Delta q_{\text{H}\alpha}$ is the difference in Mulliken charges given by

$$\Delta q_{\text{H}\alpha} = q_{\text{H}\alpha}(\text{H}_2 \cdots 4\text{Å} \cdots \text{HN}^-\text{N}^+\text{R}_3) - q_{\text{H}\alpha}(\text{H}_2 \cdots 4\text{Å} \cdots \text{H}_2) \quad (5)$$

After separately optimizing the geometries of H_2 and $\text{HN}^-\text{N}^+\text{R}_3$ molecules at the HF/6-31G* level,²⁰ a single-point HF/6-31G* calculation is performed for the model **1**.



The resonance constant σ_{R} is calculated from the overall π -electron transfer ($\sum \Delta q_{\pi}$) between $\text{R}_3\text{N}^+\text{N}^-$ and the ethylene π system of **2** by the equation

$$\sigma_{\text{R}} = 4.167 \sum \Delta q_{\pi} - 0.06083 \quad (6)$$

We optimize the geometry of ethylene at the HF/4-31G level^{20a-c} and then the geometry of $\text{R}_3\text{N}^+\text{N}^-$ in **2** (the ethylene skeleton is kept frozen) at the same level. After a Mulliken population analysis, $\sum \Delta q_{\pi}$ is calculated as the difference between the total π -electron population on the two carbon atoms in **2** and in the parent ethylene.

The electronegativity constant σ_{χ} is based upon the

Mulliken H atom charge in $\text{R}_3\text{N}^+\text{N}^-\text{H}$. 6-31G**//6-31G* calculations on the $\text{R}_3\text{N}^+\text{N}^-\text{H}$ and CH_4 molecules give the charge transferred through the H— $\text{N}^-\text{N}^+\text{R}_3$ sigma bond compared with that for H— CH_3 . The respective equation is

$$\sigma_{\chi} = 2[q_{\text{H}}(\text{HN}^-\text{N}^+\text{R}_3) - q_{\text{H}}(\text{CH}_4)] \quad (7)$$

First-order hyperpolarizability calculations. For computational feasibility, this study was performed at the restricted Hartree–Fock level with 6-31G** basis set²⁰ A full geometry optimization was carried out in all cases employing Berny's optimization algorithm.²¹ The first-order polarizability β is the second-order response of the dipole moment with respect to the external electric fields:

$$\mu_i = \mu_i^0 + \sum_j \alpha_{ij}(-\omega_0; \omega_1) E_j(\omega_1) + \frac{1}{2} \sum_{jk} \beta_{ijk}(-\omega_0; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) + \dots \quad (8)$$

where

$$\omega_0 = \sum_{\xi} \omega_{\xi} \quad (9)$$

and the summations are running over the field subscripts j and k , associated with the cartesian coordinates.

The coupled-perturbed Hartree–Fock (CPHF) procedure²² was used for computing *ab initio* static electronic hyperpolarizabilities $\beta(0;0,0)$. In this approach a term representing the interaction between the external static field and the molecular dipole is added to the Fock matrix. Its effect on the density matrix is obtained by expanding the CPHF equation as a power series in the field amplitude, and by solving it self-consistently order by order. The successive density matrix derivatives are used to evaluate the electronic hyperpolarizability components.

$\beta(0)$, the norm of the vector part of the β tensor, was computed using the equation

$$\beta(0) = \left(\sum_i \beta_i^2 \right)^{1/2} \quad (10)$$

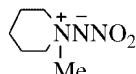
with

$$\beta_i = \beta_{iii} + \sum_{j \neq i} \beta_{ijj} \quad (11)$$

where i, j are the cartesian coordinates x, y, z .

The use of a larger basis set and inclusion of correlation effects might give better absolute values of first-order hyperpolarizabilities. However, we are only interested in a comparison of trends in $\beta(0;0,0)$ between

Table 1. Hydrogen-bond basicity (pK_{HB}) of MeA, Me₂NA and R₃N⁺N⁻A molecules (A = CPh, C≡N, SO₂R and NO₂)

A	MeA (pK _{HB})	Δ ₁ pK _{HB} ^a	Me ₂ NA(pK _{HB})	Δ ₂ pK _{HB} ^b	R ₃ N ⁺ N ⁻ A(pK _{HB})
COPh	MeCOPh (1.11) ²⁴	+1.12 →	Me ₂ NCOPh (2.23) ²⁵	+0.83 →	Me ₃ N ⁺ N ⁻ COPh (3.06) ²⁶
C≡N	MeC≡N (0.91) ²⁷	+0.65 →	Me ₂ NC≡N (1.56) ²⁷	+1.68 →	Bu ₃ N ⁺ N ⁻ C≡N (3.24) ¹³
NO ₂	MeNO ₂ (0.27) ¹⁵	+0.55 →	Me ₂ NNO ₂ (0.82) ¹⁵	+1.09 →	 (1.91) ¹⁵
SO ₂ R	MeSO ₂ Me (1.40) ¹⁴	-0.10 →	Me ₂ NSO ₂ Me (1.30) ¹⁴	+1.60 →	Me ₃ N ⁺ N ⁻ SO ₂ Oct (2.90) ¹⁴

Δ₁pK_{HB} = pK_{HB}(Me₂NA) - pK_{HB}(MeA).

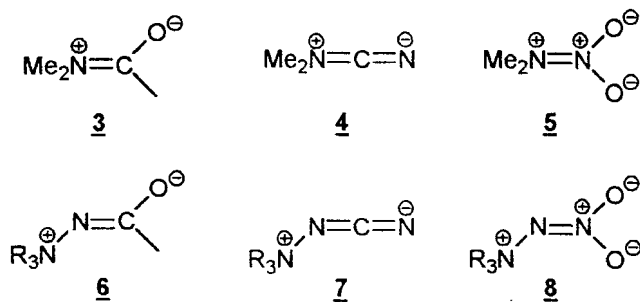
Δ₂pK_{HB} = pK_{HB}(R₃N⁺N⁻A) - pK_{HB}(Me₂NA).

two series of push-pull molecules, where the hyperpolarizability is dominated by a single term.²³ Hence we expect obtaining reliable trends with the less sophisticated method used here.

RESULTS AND DISCUSSION

Hydrogen-bond basicity

The basicity data given in Table 1 show the well-known higher basicity of amides, cyanamides and nitramides compared respectively with ketones, nitriles and nitroalkanes, which is often explained as a result of delocalization of the nitrogen lone pair electrons (resonance structures 3–5), with a resultant higher electron density on the carbonyl oxygen (3), the nitrile nitrogen (4) and nitro oxygen (5), respectively.



On changing the Me₂N group to an R₃N⁺N⁻ group, we obtain *N*-trialkylammonioamidate, -cyanamidate, -nitramidate or -sulfonamidate (the nomenclature of R₃N⁺N⁻A compounds is varied.²⁸ The 'amidate nomenclature,' given in Table 2, will be used here in order to compare easily amidates with amides, cyanamidates with cyanamides, etc.), which are still more basic by 0.83–1.60 pK units (Table 1). Therefore, R₃N⁺N⁻ appears a much stronger electron donor group than

R₂N. The main interaction mechanism with the acceptor function is probably the resonance effect (canonical structures 6–8) for COR, C≡N and NO₂. Towards SO₂R, R₃N⁺N⁻ is undoubtedly also a better electron donor group than R₂N, but the interaction mechanism(s) remain(s) unclear since sulfonamides are less basic than sulfones (see Table 1).

Infrared group frequencies

To the extent that the CO, C≡N, NO and SO bonds can be approximated as diatomic vibrators, or that mechanical effects are subtracted in the difference, the infrared shifts, Δν, in Table 3 can be considered to reflect the electronic substituent effect on the CO, C≡N, NO and SO force constants. The Gordy²⁹ and Siebert³⁰ empirical equations show that the force constants of multiple bonds depend markedly on the bond order. We therefore interpret the negative infrared shifts in Table 3 as the consequence of a decrease of the CO, C≡N, and NO bond orders. The resonance structures 3–8 predict this bond order decrease. The greater shifts for R₃N⁺N⁻A with respect to R₂NA compounds again reveal that R₃N⁺N⁻ is by far the strongest resonance group. Also the interaction mechanism(s) of R₃N⁺N⁻ with the sulfonyl function cannot be easily revealed by the 72 cm⁻¹ shift from sulfonamide to sulfonamidate since sulfonamides have higher SO₂ stretching frequencies than sulfones (see Table 3).

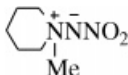
Table 2. Names of R₃N⁺N⁻A compounds

R ₃ N ⁺ N ⁻ COR	<i>N</i> -Trialkylammonioamidate ^a
R ₃ N ⁺ N ⁻ C≡N	<i>N</i> -Trialkylammoniocyanamidate
R ₃ N ⁺ N ⁻ NO ₂	<i>N</i> -Trialkylammonionitramidate
R ₃ N ⁺ N ⁻ SO ₂ R	<i>N</i> -Trialkylammoniosulfonamidate ^b

^aFor example, Me₃N⁺N⁻COPh is *N*-trimethylammoniobenzamidate.

^bMe₃N⁺N⁻SO₂Oct is *N*-trimethylammoniooctanesulfonamidate.

Table 3. Infrared group frequencies (cm^{-1}) of MeA, Me₂NA and R₃N⁺N⁻A molecules (A = COMe, C≡N, NO₂ and SO₂R)^a

Stretching vibration	A	MeA (ν)	$\Delta\nu_1^b$	Me ₂ NA (ν)	$\Delta\nu_2^c$	R ₃ N ⁺ N ⁻ A (ν)
$\nu(\text{C}=\text{O})$	COMe	MeCOMe (1712) ^e	$\xrightarrow{-71}$	Me ₂ NCOMe (1641) ^e	$\xrightarrow{-58}$	Me ₃ N ⁺ N ⁻ COPh (1583) ^e
$\nu(\text{C}\equiv\text{N})$	C≡N	MeC≡N (2255)	$\xrightarrow{-34}$	Me ₂ NCN (2221)	$\xrightarrow{-117}$	Bu ₃ N ⁺ N ⁻ C≡N (2104)
$\nu(\text{NO}_2)^d$	NO ₂	MeNO ₂ (1470)	$\xrightarrow{-52}$	Me ₂ NNO ₂ (1418)	$\xrightarrow{-77}$	 (1341)
$\nu(\text{SO}_2)^d$	SO ₂ R	MeSO ₂ Me (1239)	$\xrightarrow{+16}$	Me ₂ NSO ₂ Me (1255)	$\xrightarrow{-72}$	Me ₃ N ⁺ N ⁻ SO ₂ Oct (1183) ^f

^a This work. Values for CCl₄ solutions unless stated otherwise.

^b $\Delta\nu_1 = \nu(\text{Me}_2\text{NA}) - \nu(\text{MeA})$.

^c $\Delta\nu_2 = \nu(\text{R}_3\text{N}^+\text{N}^-\text{A}) - \nu(\text{Me}_2\text{NA})$.

^d $(\nu_{\text{as}} + \nu_{\text{s}})/2$.

^e In CH₂Cl₂.

^f In 1,2-dichloroethane

Interestingly, ΔpK_{HB} (Table 1) and $\Delta\nu$ (Table 3) are significantly correlated:

$$\Delta pK_{\text{HB}} = 0.112(-\Delta\nu) + 0.01 \quad (n = 8, r = 0.925, s = 0.24) \quad (12)$$

where n is the number of data, s the standard deviation and r the correlation coefficient, and the most deviant point corresponds to *N*-trimethylammoniooctanesulfonamide. When this compound is excluded, r rises to 0.979 and s falls to 0.12. With this exception, electronic effects appear to operate similarly on the two properties. For example, the greatest ΔpK_{HB} (+1.68) and $\Delta\nu$ (-117 cm^{-1}) occur for *N*-tributylammoniocyanamidate compared with *N,N*-dimethylcyanamide. This probably

results from the much stronger resonance effect of Bu₃N⁺N⁻ over Me₂N with the nitrile function (i.e. a higher contribution of **7** than **4** to the structure), giving both a higher nitrile nitrogen electronic density and a lower C≡N bond order. In this connection we note that the C≡N stretching frequency (2104 cm^{-1}) of Bu₃N⁺N⁻C≡N is very close to that (2080 cm^{-1}) of the carbanion in the dimer³¹ [Bu₄N⁺, Ph(Me)C⁻C≡N]₂.

Bond lengths and bond angles

If R₃N⁺N⁻ is a better resonance electron donor than Me₂N, the canonical structures **6–8** must contribute more importantly than **3–5** to the description of molecules. In terms of geometry, the XN⁻ bonds must be shorter in *N*-

Table 4. Comparison of bond lengths (\AA , x-ray results)¹⁷ in Me₂NA and Me₃N⁺N⁻A compounds (A = CPh, 4-MeC₆H₄SO₂, NO₂)

Compound	Refcod ^a	Ref.	$\frac{d(\text{XN}^-)^b}{d(\text{XN})^b}$	Δd_1^c	$d(\text{XO})^b$	Δd_2^d
Me ₃ N ⁺ N ⁻ COC ₆ H ₅	TMABZA10	32	1.313 (6)		1.243 (5)	
Me ₂ NCOC ₆ H ₄ -3-R ^g	CXBTZE20	35	1.348 (7)	-0.035 (13)	1.230 (7)	+0.013 (12)
Me ₃ N ⁺ N ⁻ NO ₂	TMANIA10	32	1.323 (8)		1.259 (16) ^f	
Me ₂ NNO ₂	— ^e	34	1.341 (4)	-0.018 (12)	1.232 (4) ^f	+0.027 (20)
Me ₃ N ⁺ N ⁻ SO ₂ C ₆ H ₄ -4-Me	MATOLS	36	1.592 (2)		1.445 (4) ^f	
Me ₂ NSO ₂ C ₆ H ₄ -4-Me	GESSUS	37	1.614 (2)	-0.022 (4)	1.429 (5) ^f	+0.016 (9)

^a Reference code in the CSD database.¹⁷

^b X = C, N or S.

^c $\Delta d_1 = d(\text{XN}^-) - d(\text{XN})$.

^d $\Delta d_2 = d[(\text{N}^-)\text{XO}] - d[(\text{N})\text{XO}]$.

^e Average of three x-ray structures, METNAM 01–03, with libration correction.

^f Average of the two XO distances.

^g The *meta* R substituent is:

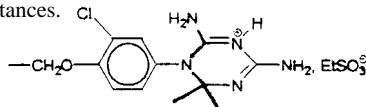
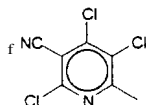
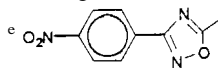


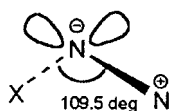
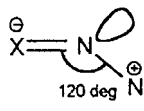
Table 5. Geometry of the R₃N⁺N⁻ groups attached to various moieties A

A	X ^a	Refcod ^b	Ref.	θ (°) ^c	d(N ⁻ N ⁺) (Å)
SO ₂ C ₆ H ₄ -4-Me	S	MATOLS	36	118.0(1)	1.471(3)
NO ₂	N	TMANIA10	32	115.0(5)	1.470(8)
COC ₆ H ₅	C	TMABZA10	32	114.2(3)	1.471(5)
^e	C	PABDIF	38	113.0(4) ^d	1.469(6) ^d
^f	C	PODXUB	39	116.1(3)	1.476(5)

^a First atom of the A moiety.^b Reference code in the CSD database.¹⁷^c XN⁻N⁺ angle.^d Average distance for two independent molecules.

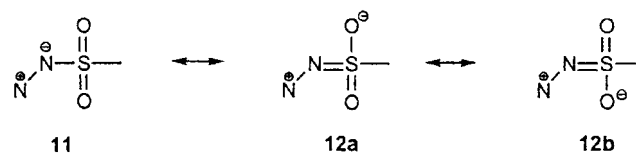
trialkylammonioamidates, -cyanamidates and -nitramidates than the XN bonds in amides, cyanamides and nitramides. Moreover, the CO, C≡N and NO bonds must be longer. Table 4 shows the CN⁻ and NN⁻ shortening (about 0.03 and 0.02 Å) and the CO and NO lengthening (about 0.01 and 0.03 Å). This confirms the greater importance of **6** and **8** with respect to **3** and **5**, i.e. the greater resonance effect of R₃N⁺N⁻ than Me₂N towards carbonyl and nitro groups (there was no response in the CSD base for any cyanamidate structure). Table 4 also shows that SN⁻ bonds are shorter than SN bonds by about 0.02 Å, and (N⁻)SO bonds longer than (N)SO bonds by about the same quantity (see below).

The data in Table 5 show clearly that the geometry of the R₃N⁺N⁻ group does not depend much on the nature of the electron-withdrawing moiety to which it is attached. The XN⁻N⁺ bond angle spans only from 113 to 118° (113 to 116° for the CN⁻N⁺ angle) and the N⁻N⁺ bond distance is close to 1.471 Å. The angle would be 109.5° if the anionic nitrogen had tetrahedral hybridization (**9**) and 120° if sp² hybridized (**10**).

**9****10**

The values in Table 5 indicate once more the importance of canonical structure **10**, at least when X is carbon or nitrogen. When X is sulfur, the properties of *N*-(trimethylammonio)toluene-*p*-sulfonamidate (MATOLS in Tables 4 and 5) might result in a significant contribution of **12**. Such a contribution might explain the 118° SN⁻N⁺ bond angle and the longer SO bonds, the higher oxygen electron density (i.e. basicity) and the

lower SO bond order (i.e. SO stretching frequency) than for the related sulfonamide.



It is possible that the nitrogen p_π-sulfur d_π overlap occurs at the expense of the oxygen p_π-sulfur d_π overlap and is efficient only with an anionic nitrogen, i.e. in sulfonamidates but not in sulfonamides. We must recall here that the lower basicity and higher SO stretching frequency of sulfonamides with respect to sulfones (Tables 1 and 3) support the absence of resonance electron donation of Me₂N to the sulfonyl group in sulfonamides.

Electronic substituent constants

Topsom¹¹ has advanced specific model systems intuitively related to field,⁴⁰ resonance³³ and electronegativity⁴¹ substituent effects. We have used this purely theoretical approach to electronic effects in order to evaluate quantitatively the possible interaction mechanisms of the R₃N⁺N⁻ substituent. Our calculated field substituent constants σ_F, resonance substituent constants σ_R and electronegativity substituent constants σ_χ are listed, and compared with those of the Me₂N substituent, in Table 6.

Our results confirm that the main interaction mechanism of R₃N⁺N⁻ is the resonance effect. R₃N⁺N⁻ has the most negative σ_R value (~-0.91) currently known⁷ in non-anionic substituents, and is more π-electron donating than Me₂N by 0.34 σ_R unit. The field effect is a second

Table 6. Values of substituent constants σ_F , σ_R and σ_χ for $R_3N^+N^-$ ^a and Me_2N ^b groups

Substituent	σ_F	σ_R	σ_χ
$N^-N^+H_3$	-0.06	-0.92	+0.19
$N^-N^+Me_3$	-0.04	-0.91	+0.17
$N^-N^+Bu_3$	-0.08	-0.90	+0.17
NMe_2	+0.17	-0.57	+0.34
H	0	0	0

^a This work.^b Ref. 19.

important mechanism. $R_3N^+N^-$ substituents have the most negative σ_F values (~ -0.06) currently known⁷ in non-anionic organic substituents, and stabilize positive charges whereas Me_2N ($\sigma_F = +0.17$) destabilizes them. Hence, in contrast to Me_2N , the resonance electron-donor effect ($\sigma_R < 0$) of $R_3N^+N^-$ is not attenuated by the field effect (σ_F is also negative).

Many data suggest⁴¹ that electronegativity effects would only be important at measurement sites close to the substituent. Such might be the case in $R_3N^+N^-A$ and Me_2NA where the substituent is contiguous to the function. In this context, we note that $R_3N^+N^-$ is less σ -electron withdrawing than Me_2N by 0.17 σ_χ unit.

On the whole, the unique electron-donor property of $R_3N^+N^-$ substituents originates not only in a very strong resonance effect but also in a cooperating field effect and, possibly, in a low electronegativity effect.

Hyperpolarizability

Organic materials with quadratic non-linear optical (NLO) properties have been the subject of intense research owing to their larger non-linearity as compared with inorganic compounds.⁴² Particular emphasis has

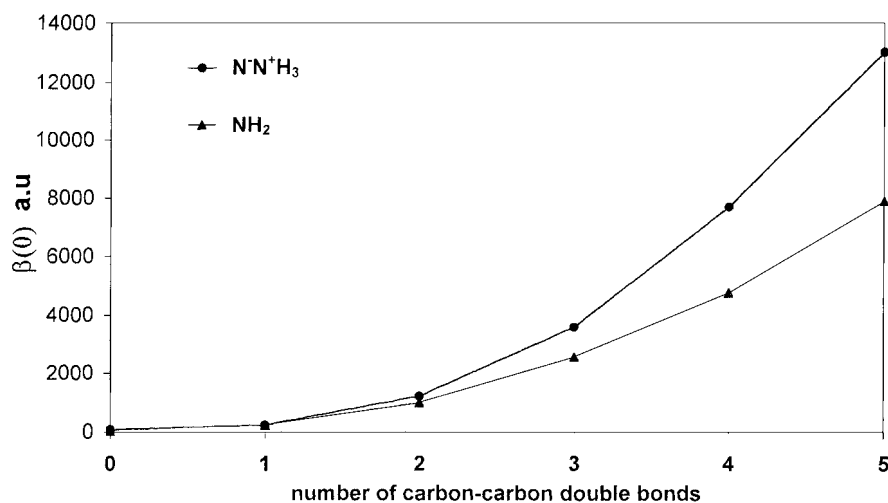
Table 7. Calculated average carbon-carbon double bond distances (\AA) in $X(CH=CH)_nNO_2$ molecules ($n = 1-5$), ($X = NH_2$ or $N^-N^+H_3$)

X	n				
	1	2	3	4	5
$-NH_2$	1.337	1.333	1.333	1.333	1.333
$-N^-N^+H_3$	1.366	1.353	1.349	1.345	1.342

been put on intramolecular charge-transfer compounds having both electron-donating and electron-accepting groups at the ends of various conjugated systems (push-pull molecules). It is well known that β values increase with (i) the strength of electron-donating and/or electron-accepting groups and (ii) the length of the π conjugated system. Some of the materials investigated so far contain amino or dialkylamino at the donor sites. In this part we wish to report on the potential of $R_3N^+N^-$ substituent as a new donor group in NLO push-pull molecules.

With the intent of comparing the efficiencies of $H_3N^+N^-$ and amino groups, we calculated static first-order hyperpolarizability $\beta(0;0,0)$ in two series of molecules, $NH_2(CH=CH)_nNO_2$ and $H_3N^+N^-(CH=CH)_nNO_2$ with $n = 1-5$. The results are collected in Fig. 1. Figure 1 confirms that the β values increase with the length of the π conjugated systems in both series. The figure clearly demonstrates that the $H_3N^+N^-$ group induces larger β values than amino group when the length of the conjugated path increases. For example, the $\beta[H_3N^+N^-(CH=CH)_5NO_2]$ value is about 1.6 times larger than the $\beta[NH_2(CH=CH)_5NO_2]$ value.

The average carbon-carbon double bond distances of both series, given in Table 7, also show that for the $H_3N^+N^-$ substituent conjugation effects are more

**Figure 1.** Calculated hyperpolarizability values (a.u.) as a function of the number of carbon-carbon double bonds: comparison of the $H_3N^+N^-(CH=CH)_nNO_2$ and $H_2N(CH=CH)_nNO_2$ series ($n = 1-5$)

important than for the NH₂ substituent, in agreement with the stronger resonance effect of H₃N⁺N⁻.

CONCLUSION

R₃N⁺N⁻ groups appear to be the strongest electron donors in uncharged organic substituents. This observation opens a large synthetic field for new push-pull molecules R₃N⁺N⁻—T—A for non-linear optics. Push-pull systems are also part of a number of pharmacophores, e.g. the antithyroid thiourea or the antibiotic 4-aminobenzensulfonamide types. Replacement of the amino group(s) by R₃N⁺N⁻ group(s) in these pharmacophores might furnish interesting new therapeutic agents.

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