Table VIII. Anisotropic Temperature Factors for Methyl Ethylene Phosphate

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P(1)	0.0067 (3)[a]	0.0153 (7)	0.0134 (4)	−0.001 (1)	0.0049 (5)	−0.002 (2)
O(2)	0.011 (1)	0.032 (3)	0.007 (1)	0.007 (3)	0.002 (2)	−0.001 (3)
O(3)	0.0072 (9)	0.032 (3)	0.011 (1)	0.005 (2)	0.007 (2)	−0.006 (3)
O(4)	0.0055 (9)	0.023 (3)	0.021 (2)	0.001 (2)	0.010 (2)	−0.003 (4)
O(5)	0.017 (1)	0.015 (2)	0.034 (3)	−0.007 (4)	0.021 (4)	0.001 (5)
C(6)	0.010 (1)	0.029 (5)	0.014 (2)	0.013 (4)	0.009 (3)	0.006 (5)
C(7)	0.011 (1)	0.029 (4)	0.013 (2)	0.005 (4)	0.013 (3)	0.000 (5)
C(8)	0.011 (2)	0.019 (5)	0.027 (3)	−0.002 (5)	0.019 (4)	0.005 (7)

[a] The standard deviation in the last significant figure is given in parentheses.

A special acknowledgment is due in this Appendix to K. N. Trueblood, who raised questions which led us to further refine this structure. We also acknowledge that Newton, Cox, and Bertrand[16] have already pointed out the typographical omission of the minus sign on the y coordinate of atom O_5.

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(16) M. G. Newton, J. R. Cox, Jr., and J. A. Bertrand, *J. Am. Chem. Soc.*, **88**, 1503 (1966).

Molecular Conformations in Highly Crowded Molecules. Electronic Spectra of Some N-Alkyl and Poly-N-alkyl Derivatives of 1,3-Diamino-2,4,6-trinitrobenzene[1]

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Abstract: Absorption spectra of 1,3-diamino-2,4,6-trinitrobenzene (**3**) and its N-alkyl, N,N- and N,N′-dialkyl, and N,N,N′,N′-tetraalkyl derivatives are related to those of simpler nitro- and polynitroanilines. On the basis of spectral displacements on N-alkylation, probable preferred conformations are suggested for a number of these compounds. Spectral "band splitting" which is observed in **3** and many of its derivatives is thought to arise from electronic transitions which have parallel geometries but opposite charge displacements upon promotion to the electronic excited states. The phenomena *steric enhancement of resonance* and *electronic butressing* are shown to be operative in this series.

In earlier papers we invoked phenomena characterized as *steric enhancement of resonance*[2] and *electronic buttressing*,[3] together with more classical steric and electronic effects, to explain changes in positions and intensities of maximal absorption in the spectra of ring- and N-substituted derivatives of 2,4-dinitroaniline (**1**)[3] and 2,4,6-trinitroaniline (**2**).[4,5] Additionally, we reported attempts to deduce from these spectra some aspects of molecular conformation which had, in at least one instance,[5,6] been confirmed by a total crystal structure determination.[7] We address ourselves now to the question of how these phenomena affect spectra and conformations in the N-alkyl, N,N- and N,N′-dialkyl, and N,N,N′,N′-tetraalkyl derivatives of 1,3-diamino-2,4,6-trinitrobenzene (**3**). This series of compounds allows an interesting test of how the opposing influences of strong resonance interactions and progressively increasing substituent bulk affect coplanarity of individual substituents with the ring in highly crowded molecules.

Band Assignments for 1,3-Diamino-2,4,6-trinitrobenzene (3). With the polynitroanilines discussed earlier,[3,4] ultraviolet spectra in methanol above 250 mμ were characterized by two medium-to-high-intensity $V \leftarrow N$ maxima (incompletely resolved in the case of **1**),[8] for which band assignments were relatively straightforward. Single medium-intensity bands, showing maxima near 400 mμ, result from *ortho* electronic interactions in 2-nitroaniline and 2,6-dinitroaniline; these positions are shifted only slightly by a variety of ring substituents. Bands of similar intensity and position of absorption (band 2) appear in the two-band systems of both **1** and **2** (Table I, Figure 1), and thus may be considered to arise from $[H_2{}^+N{=}C(1) \rightarrow C(2){=}NO_2{}^-]$ electronic transi-

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(1) Part V in the series, "Steric Enhancement of Resonance."

(2) M. J. Kamlet, J. C. Hoffsommer, and H. G. Adolph, *J. Am. Chem. Soc.*, **84**, 3925 (1962); H. G. Adolph, B. Johnson, and M. J. Kamlet, *J. Org. Chem.*, 30, 2864 (1965).

(3) M. J. Kamlet, H. G. Adolph, and J. C. Hoffsommer, *J. Am. Chem. Soc.*, **86**, 4018 (1964).

(4) M. J. Kamlet, J. C. Hoffsommer, R. R. Minesinger, and H. G. Adolph, *J. Org. Chem.*, **33**, 3070 (1968).

(5) M. J. Kamlet, R. R. Minesinger, J. C. Hoffsommer, J. C. Dacons, and H. G. Adolph, *J. Chem. Soc.*, *B*, 1147 (1968).

(6) C. Dickinson, J. R. Holden, and M. J. Kamlet, *Proc. Chem. Soc.*, 232 (1964).

(7) C. Dickinson, J. M. Stewart, and J. R. Holden, *Acta Cryst.*, **21**, 663 (1966).

(8) Strong band overlap in **1** (Figure 1) probably shifts band 1 bathochromically and band 2 hypsochromically from their "true" positions.

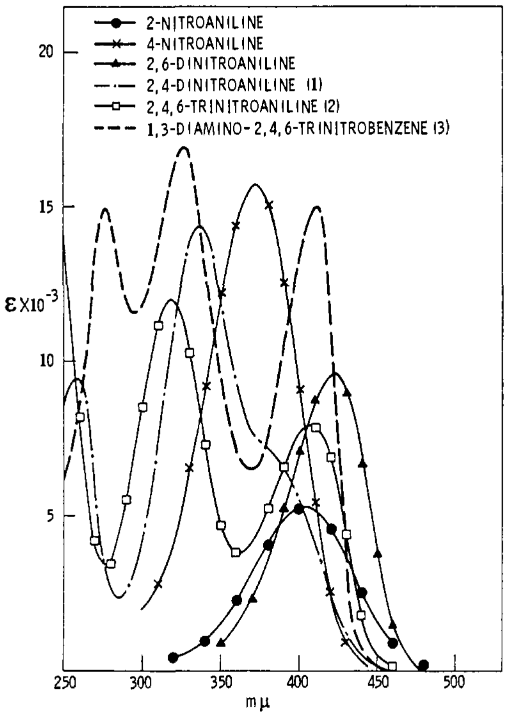
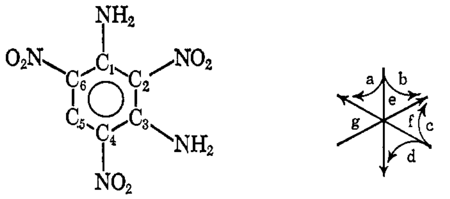


Figure 1. Absorption spectra of some mono- and polynitroanilines and 1,3-diamino-2,4,6-trinitrobenzene.

tions analogous to those in 2-nitro- and 2,6-dinitroaniline. A regular progression toward shorter wavelengths and lower intensities was observed from 371 mμ (ε 15,750) for the single-band maximum in 4-nitroaniline to 336 mμ (ε 14,400)[8] for band 1 of **1** to 318 mμ (ε 12,000) for band 1 of **2**. Since this trend reflected a general hypsochromic–hypochromic effect of electron-withdrawing 2-substituents on 4-nitroaniline spectra, it was taken as evidence that these shorter wavelength components of the 2,4-di- and 2,4,6-trinitroaniline spectra derived from $[H_2^+N{=}C(1) \rightarrow C(4){=}NO_2^-]$ electronic transitions.[9]

Band attributions are not so clear-cut with 1,3-diamino-2,4,6-trinitrobenzene (**3**), which differs significantly from the monoaminopolynitrobenzenes in that *three* distinct high-intensity maxima contribute to the spectral envelope in the region of interest: band 1a, λ_{max} 276 mμ (ε 14,900); band 1b, λ_{max} 326 mμ (ε 16,900); band 2, λ_{max} 411 mμ (ε 14,900). The 411-mμ maximum is close in position and has about doubled intensity relative to band 2 of **2**. Hence, from reasoning such as applied in the earlier instances, we have no qualms in delegating this band to the $[H_2^+N{=}C(1) \rightarrow C(2){=}NO_2^-]$ electronic transition arising from four near-equivalent *ortho* amine → nitro interactions (1 → 2, 1 → 6, 3 → 2, 3 → 4; represented by a–d in Figure 2).

The question arises, however, as to whether the 276-mμ band or the 326-mμ band or both derive from the two exactly equivalent *para* amine → nitro interactions (1 → 4, 3 → 6; e and f in Figure 2); if one or the other of these maxima is assigned to the $[H_2^+N{=}C(1) \rightarrow C(4){=}NO_2^-]$ electronic transition, what is the origin of the "extraneous" band?



3

Figure 2.

Milliaresi and coworkers[10] have suggested that the $[H_2^+N{=}C(1) \rightarrow C(4){=}NO_2^-]$ assignment belongs to the 326-mμ maximum and that the shorter wavelength band arises from a "nitrobenzene chromophore" uninfluenced by direct resonance interaction with amine, *i.e.*, in compound **3** a $[^+C(5) \rightarrow C(2){=}NO_2^-]$ electronic transition (represented by g in Figure 2). The latter assignment for the "extraneous" band was not unreasonable in the light of information available to these earlier workers; medium-to-high-intensity maxima, otherwise unaccounted for and seemingly of similar derivation, were observed also in the spectra of **1** at 257 mμ, 2-nitroaniline at 276 mμ, 2,6-dinitroaniline at 252 mμ, and 1,3-diamino-2,4-dinitroaniline at either 247 or 295 mμ.[10,11] Early in the present investigation, however, it was found that mono- and poly-N-alkylation of **3** caused changes in position and intensity of the 276-mμ band (discussed below) which were completely inconsistent with Milliaresi's interpretation. For present purposes an alternative set of attributions for the 276 and 326 mμ maxima of **3** was required.

Our approach to the question of band assignments involved an *ab initio* attempt to judge where λ_{max} for the $[H_2^+N{=}C(1) \rightarrow C(4){=}NO_2^-]$ band in **3** should appear. The operating assumption was that similar substituents should cause parallel shifts of corresponding maxima in pairs of closely related compounds. Thus, it might be expected that introduction of a third nitro substituent should cause like displacements in bands attributable to *para* interactions on going from 2,4-dinitroaniline (**1**) to 2,4,6-trinitroaniline (**2**) and from 1,3-diamino-4,6-dinitrobenzene (**4**) to 1,3-diamino-2,4,6-trinitrobenzene (**3**). From λ_{max} 336 mμ (29,760 cm^{-1}) for band 1 of **1** to λ_{max} 318 mμ (31,450 cm^{-1}) for band 1 of **2**, the displacement is +1690 cm^{-1}. A similar hypsochromic shift of the corresponding band from **4**, λ_{max} 321 mμ (31,150 cm^{-1}), to **3** would lead us to expect a maximum near 32,840 cm^{-1} (304 mμ). Alternatively, it might be assumed that introduction of the second amine group on going from **1** to **4** and from **2** to **3** should cause like displacements of maxima. From **1** to **4** the band-1 λ_{max} shifts by +1390 cm^{-1}; a blue shift of comparable magnitude from **2** to **3** would again lead to λ_{max} near 32,840 cm^{-1} (304 mμ). Both sets of comparisons result in a predicted maximum for **3** about midway between the observed band 1a and band 1b.

From such reasoning we conclude that both band 1a and band 1b of **3** derive from the *para* amine → nitro interactions, *i.e.*, the $[H_2^+N{=}C(1) \rightarrow C(4){=}NO_2^-]$ electronic transition. We adopt as a working hypothesis

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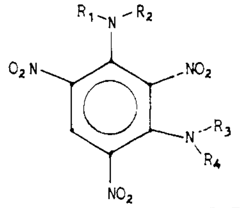
[9] That angles of twist of individual nitro groups, deduced from the spectrum of 2,3,4,6-tetranitroaniline on the above assumptions, agreed with values from a total crystal structure determination,[5-7] served as confirmation for these band assignments.

[10] E. E. Milliaresi, V. V. Efremov, and V. A. Ismailskii, *Dokl. Akad. Nauk SSSR*, **179**, 349 (1968).

[11] A weakness in the Russian workers' explanation was the failure to account for the complete absence of any spectral feature attributable to such an electronic transition in the spectrum of **2**.[10]

Table I. Absorption Spectra of Alkyl Derivatives of 1,3-Diamino-2,4,6-trinitrobenzene and Related Compounds. Solvent Methanol.



					Band-1a			Band-1b			Band-2		
No.	R_1	R_2	R_3	R_4	λ_{max}, mμ	ν_{max}, cm^{-1}	log ε	λ_{max}, mμ	ν_{max}, cm^{-1}	log ε	λ_{max}, mμ	ν_{max}, cm^{-1}	log ε
1.	2,4-Dinitroaniline				336	29,760	4.16				(390)[a]	(25,640)	(3.81)
2.	2,4,6-Trinitroaniline				318	31,450	4.08				407	24,570	3.90
3.	H	H	H	H	276	36,230	4.17	326	30,670	4.23	411	24,340	4.17
4.	1,3-Diamino-4,6-dinitrobenzene				321	31,150	4.47				397	25,190	4.01
5.	1,3-Diamino-2,4-dinitrobenzene[b]				295	33,900	3.99	345	28,990	4.05	370 403	27,030 24,810	4.11 4.08
6.	CH_3	H	H	H	292	34,250	4.26	333	30,000	4.27	409	24,450	4.15
7.	C_2H_5	H	H	H	293	34,130	4.26	334	29,940	4.28	410	24,390	4.13
8.	iso-C_3H_7	H	H	H	297	33,670	4.27	335	29,850	4.28	408	24,510	4.08
9.	tert-C_4H_9	H	H	H	311	32,150	4.25	(335)[a]	(29,850)	(4.23)	407	24,570	4.00
10.	CH_3	H	CH_3	H	307	32,570	4.32	347	28,820	4.23	413	24,210	4.10
11.	C_2H_5	H	C_2H_5	H	308	32,470	4.34	348	28,740	4.25	413	24,210	4.08
12.	iso-C_3H_7	H	iso-C_3H_7	H	313	31,950	4.35	348	28,740	4.26	408	24,510	4.02
13.	tert-C_4H_9	H	tert-C_4H_9	H	323	30,960	4.21	(350)[a]	(28,570)	(4.13)	(410)[a]	(24,390)	(3.82)
14.	CH_3	CH_3	H	H	298	33,560	4.08	351	28,490	4.14	405	24,690	4.04
15.	C_2H_5	C_2H_5	H	H	302	33,110	4.03	358	27,930	4.12	400	25,000	4.01
16.	CH_3	CH_3	CH_3	CH_3	345	28,980	4.11						
17.	C_2H_5	C_2H_5	C_2H_5	C_2H_5	352	28,410	4.02						
18.	1,3-Bis(ethylamino)-4,6-dinitrobenzene				333	30,030	4.47				417	23,980	4.08

a) Values in parentheses are for shoulders or inflections
b) Solvent ethanol, ref. 10.

that the *para* band has been "split" into two components which appear at roughly equal energy increments on either side of the "normally expected" band-1 position. For spectra–structure correlations wherein "split" and "unsplit" $[R_2{}^+N{=}C(1) \rightarrow C(4){=}NO_2{}^-]$ transition maxima are compared, we adopt a "weighted" midpoint between band 1a and band 1b as the band-1 λ_{max} of **3** and its N-alkyl derivatives. It is significant to this hypothesis that, in comparing **3** with its N-alkyl and poly-N-alkyl derivatives, displacements of band 1a and band 1b, although not always of similar magnitudes, are always in similar directions (Table I, Figures 3–5).

Structural Requirements for "Band Splitting." To invoke "band splitting" in the spectra of **3** and its N-alkyl derivatives, but not in the instances of **1**, **2**, or their N-alkyl derivatives, would be to imply the operation of a hitherto unencountered phenomenon, attributable to some element of structural dissimilarity. An obvious difference, the presence of a second strongly conjugating electron-releasing substituent *meta* to the first, seems, from limited information,[12] to be a necessary *but not sufficient* condition for "band splitting;" 1,3-diamino-4,6-dinitrobenzene (**4**) exhibits an uncomplicated two-band spectrum (Table I, Figure 4), with the next shorter wavelength maximum at 235 mμ.

The unique element of structure may be that with **3**, for the first time, we entertain the case wherein nonequivalent electronic transitions have parallel geometries and where displacements of charge in the electronic excitations are in opposing directions (1 → 4 *vs.* 3 → 2; 3 → 6 *vs.* 1 → 2; in Figure 2, e *vs.* c, f *vs.* b).[12]

As reported by Milliaresi and coworkers,[10] 1,3-diamino-2,4-dinitrobenzene (**5**), which represents a closely analogous example involving parallel but opposed nonequivalent transitions (1 → 4 *vs.* 3 → 2), shows maxima in ethanol at 295, 345, 370, and 403 mμ (ε 9800, 11,300, 12,800, and 12,100). It is attractive to consider that the 295- and 345-mμ maxima of **5** correspond to bands 1a and 1b of **3** and that, as with **3**, they arise from "splitting" of a $[H_2{}^+N{=}C(1) \rightarrow C(4){=}NO_2{}^-]$ band (which might "normally" have been expected at *ca.* 318 mμ). Indeed, if we accept that these maxima do represent correspondingly "split" components of band 1, the displacements from 295 mμ in **5** to 277 mμ[13] for band 1a of **3** and from 345 mμ in **5** to 327 mμ[13] for

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[12] In an earlier paper we commented that a comparable element of structure occurred also in 3-amino-2,4,6-trinitrophenoxide ion and that the spectrum of the latter material also showed an "extraneous" band (at 288 mμ) not evidenced in a summation of the spectra of 3 and picrate ion.[5]

[13] The positions in ethanol reported by the earlier workers[10] differ slightly from the positions in methanol (Table I).

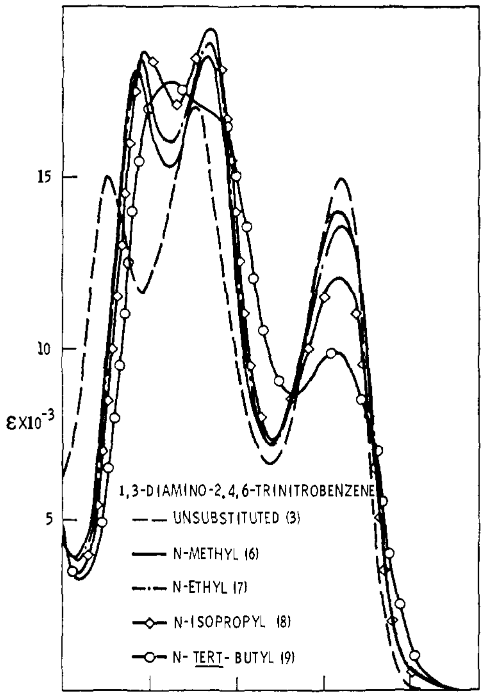


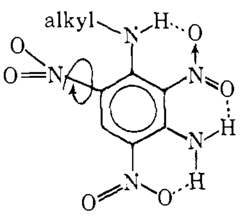
Figure 3. Absorption spectra of N-alkyl derivatives of 1,3-diamino-2,4,6-trinitrobenzene.

band 1b of **3** reflect hypsochromic shifts of +2200 and +1600 cm^{-1}, respectively, attributable to the effect of the added 6-nitro substituent. These values bracket the +1690 cm^{-1} hypsochromic effect of a 6-nitro substituent on band 1, which is observed on going from **1** to **2**. We consider that this result supports both the band assignments and the methods used to arrive thereat.[14]

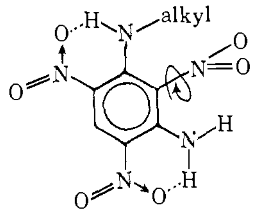
1-Alkylamino-3-amino-2,4,6-trinitrobenzenes, Possible Conformations. A total crystal structure determination[15] and earlier spectra-structure studies[3-6] furnish evidence that strong mesomeric and hydrogen-bonding forces hold all five substituents essentially coplanar with the ring in 1,3-diamino-2,4,6-trinitrobenzene (**3**). With the N-monoalkyl derivatives of **3**, a number of conformations are possible wherein loss of stabilization by conjugation and hydrogen bonding might be minimized. These should be evidenced by differing effects on spectra with progressively increasing alkyl bulk.

(A) In the unlikely event that all five substituents remained coplanar with the ring, we would expect to observe bathochromic–hyperchromic displacements of all three maxima, paralleling the effects of N-alkylation on *o*- and *p*-nitroaniline spectra. (B) The 1-alkylamino group might be twisted strongly from planarity; this might or might not impose a somewhat lesser twist on the neighboring 2- and/or 6-nitro groups (paralleling the condition around the 3 position in 2,3,4,6-tetranitroaniline).[5] If such were the conformation, the spectra with increasing alkyl bulk would change in such a manner as to resemble more closely that of 2,4,6-trinitroaniline (**2**) as influenced by substitution in the 3 position by nonconjugating substituents. Judging from spectra of 2,3,4,6-tetranitroaniline or 3,3′-diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl,[5] the effect would be hypochromic on all three bands with a tendency toward coalescence of bands 1a and 1b. (C) The 1-alkylamino group might remain coplanar, with the alkyl disposed toward the 6-nitro substituent and forcing the latter increasingly from planarity. In such an instance the trend should be toward approximating more closely the spectrum of 1,3-diamino-2,4-dinitrobenzene (**5**),[10] *i.e.*, strong decreases in band-1a and band-1b intensities, lesser decreases in band-2 intensities, a tendency toward increased fine structure in band 2. (D) A coplanar 1-alkylamine substituent might have the alkyl group disposed in the direction of the 2-nitro substituent. As the latter was forced increasingly from planarity with increasing alkyl bulk, we would expect a series of spectra which increasingly resembled that of 1,3-diamino-4,6-dinitrobenzene (**4**), *i.e.*, bathochromic–hyperchromic shifts and a tendency toward coalescing of bands 1a and 1b, a hypochromic effect on band 2.

Spectra–structure studies on N-alkyl and N,N-dialkyl derivatives of **1**[3] and **2**[4] suggested strongly that, in closely related molecules, "electronically buttressed" alkylamine groups (*vide infra*) tended to remain coplanar at the expense of neighboring nitro substituents. On this basis, conformations C or D seemed the most likely *a priori* possibilities.



conformation C



conformation D

1-Alkylamino-3-amino-2,4,6-trinitrobenzenes, Spectra. Absorption spectra of 1-methylamino- (**6**), 1-ethylamino- (**7**), 1-isopropylamino- (**8**), 1-*t*-butylamino-3-amino-2,4,6-trinitrobenzene (**9**), and the parent compound **3** are compared in Figure 3 (Table I). Several unambiguous trends with increasing alkyl group bulk may readily be discerned.

Band-2 maxima for the five compounds show reasonably constant positions (409 ± 2 mμ), but a stepwise lowering of intensity from **3** to **6** to **7** to **8** to **9**. Such a trend seems clearly to illustrate the influence of progressively increasing steric inhibition of resonance on [RH$^+$N=C(1) → C(2)=NO$_2^-$] electronic transitions,

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(14) A seeming weakness in the current rationale deserves preliminary comment. If "splitting" of the *para* band arises from interaction with a parallel *ortho* transition, theory would require that the *ortho* band should be "split" in turn (private communication, Professor H. H. Jaffé, University of Cincinnati). The maxima at 370 and 403 mμ may represent the two components of such a "split" [H$_2^+$N=C(1) → C(2)=NO$_2^-$] band in **5**. With **3**, however, not even an inflection is evident on visual inspection to suggest such "splitting" of band 2. Indeed, band 2 of **3** is among the sharpest we have observed in nitroaniline spectra (see forthcoming papers on band shapes of nitrobenzene derivatives).

It is therefore highly significant to the present argument that examination of the spectra of **3** and several of its N-alkyl derivatives under a Du Pont Model 310 curve resolver in each case disclosed the existence of a completely submerged second component of band 2 with a maximum near 386 mμ. The resolved spectra of **3** and a number of analogous polyoxy-, polyamino-, and polyhydroxypolynitrobenzenes and biphenyls and the spectroscopic (rather than the structural) basis for the "splitting" phenomenon will be treated in greater detail in a subsequent offering. For present purposes, however, it suffices that the "hidden component" of band 2 does not affect our conclusions regarding substituent effects on either spectra or conformations.

(15) J. R. Holden, *Acta Cryst.*, **22**, 545 (1967).

such as was observed with the N,N-dialkyl derivatives of 1[3] and the N-alkyl and N,N-dialkyl derivatives of 2.[4]

More interesting are the effects on the band-1 components. From **3** to its N-methyl derivative **6**, displacements of both maxima are bathochromic (more so with band 1a than band 1b) and strongly hyperchromic (a 20% increase in $\epsilon_{\max}$ of band 1a, a 9% increase for band 1b); the bathochromic-hyperchromic progressions continue on going to the N-ethyl derivative **7** and the N-isopropyl derivative **8**. With the N-*t*-butyl derivative **9**, red shifts of the maxima are again observed (most readily discerned by comparing band edges), but now the effects on the absorption intensities are *hypo*chromic relative to **6–8**.

Also noteworthy are the decreased separations between band-1a and band-1b maxima. Values of $\nu_{\max}^{1a} - \nu_{\max}^{1b}$ are as follows: **3**, 5560 cm^{-1}; **6**, 4250 cm^{-1}; **7**, 4200 cm^{-1}; **8**, 3820 cm^{-1}; and with **9** the bands have merged to the extent that there appears no discrete intermediate minimum.

The displacements in band positions and intensities and the apparent tendency toward "desplitting" (band coalescence) in **6–9** represent trends toward approximating more closely the spectrum of 1,3-diamino-4,6-dinitrobenzene (**4**). On this basis, D is suggested as the preferred conformation for compounds **6–8**, *i.e.*, 3, 4, and 6 substituents approaching exact coplanarity with the ring, "essentially" coplanar 1-alkylamine substituents with the alkyl groups disposed in the direction of the 2 position, and 2-nitro substituents twisted strongly from planarity.

With compound **9**, the decreased $\epsilon_{\max}$ values relative to **6–8** for bands 1a and 1b are taken to represent effects of steric inhibition of resonance on the [RH$^+$N=C(1) → C(4)=NO$_2^-$] electronic transition. Here, crowding would appear to be excessive even with the 2-nitro substituent twisted 90° from coplanarity; the spectrum suggests that a significant twist is imposed also on the 1-*t*-butylamine substituent.

1,3-Bis(alkylamino)-2,4,6-trinitrobenzenes, Spectra and Conformations. Trends toward resembling more closely the spectrum of **4**, as substituent bulk increases through isopropyl, are even more evident with the N,N′-dialkyl derivatives of **3**. Spectra of 1,3-bis(methylamino)- (**10**), 1,3-bis(ethylamino)- (**11**), 1,3-bis(isopropylamino)- (**12**), and 1,3-bis(*t*-butylamino)-2,4,6-trinitrobenzene (**13**) are compared with **3** and **4** in Figure 4 (Table I).

The progressions, as steric requirements grow greater, follow those noted for the mono-N-alkyl derivatives. Band-2 absorption intensities decrease for **10–14** with minimal changes in position ($\lambda_{\max}$ 410.5 ± 2.5 mμ); bathochromic displacements of band-1a and band-1b maxima are accompanied by increasing absorption intensities for **10–12**, but sharply reduced $\epsilon_{\max}$ values for **13**. The tendency toward band coalescence also continues. Values of $\nu_{\max}^{1a} - \nu_{\max}^{1b}$ are as follows: **10**, 3750 cm^{-1}; **11**, 3730 cm^{-1}; **12**, 3210 cm^{-1}; and with **13**, band 1b appears only as a weak inflection in the diffuse spectral envelope.

As with **6–8**, the spectral displacements for **10–12** are most readily rationalized in terms of preferred conformations wherein only substituents involved exclusively in [RH$^+$N=C(1) → C(2)=NO$_2^-$] electronic transitions are rotated significantly from planarity, while substituents involved also in [RH$^+$N=C(1) → C(4)=NO$_2^-$] electronic transitions remain "essentially" coplanar. Among plausible rotomers, these conditions are met only in the case of conformation E, wherein the 4- and 6-nitro substituents approach "exact" coplanarity, the 1- and 3-alkylamine substituents tend to be "essentially" coplanar with both alkyl groups disposed in the direction of the 2 position, and the 2-nitro substituents are twisted strongly from planarity.

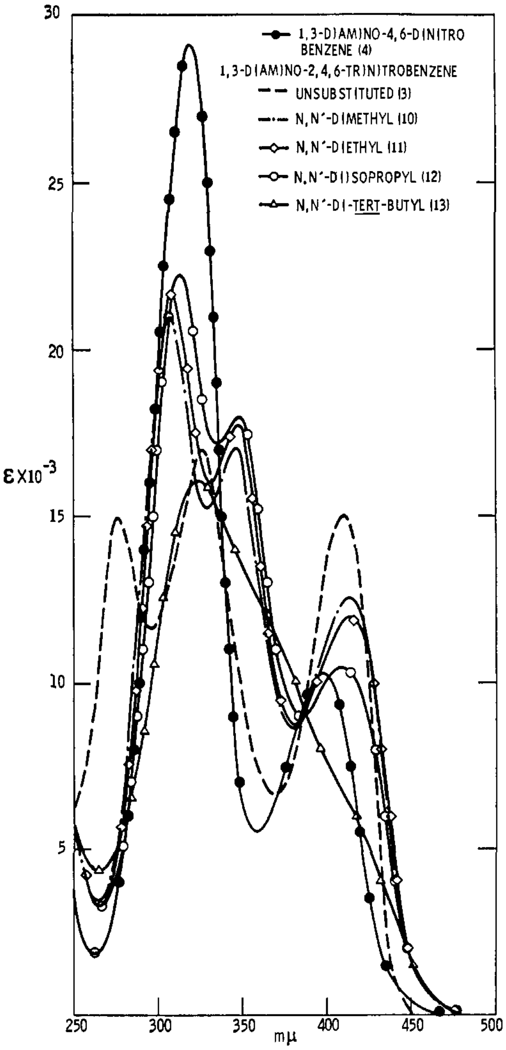
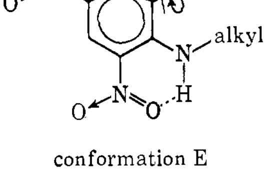


Figure 4. Absorption spectra of 1,3-diamino-4,6-dinitrobenzene and N,N′-dialkyl derivatives of 1,3-diamino-2,4,6-trinitrobenzene.



conformation E

Changes in the spectrum on going to the N,N′-bis-(*t*-butyl) derivative **13** follow the trends established by the corresponding monosubstituted compound, **9**. The strong decreases in absorption intensities of all bands are again consistent with a picture wherein crowding is excessive even with the 2-nitro group twisted 90° from planarity, and appreciable twists must additionally be imposed on the 1- and 3-*t*-butylamine substituents.

Here, however, the spectrum does not completely rule out an alternative conformer wherein one alkyl group is disposed in the direction of the 4- or 6-nitro group, and the latter, in turn, is twisted from planarity.[16]

From inspection of molecular models, appreciable crowding between alkyl groups and 90°-twisted nitro groups would result if normal aromatic bond distances and valence angles prevailed in conformation D for **6–8** and conformation E for **10–12**. Significant molecular distortions (bond-distance and valence-angle expansions and even slight folding of the aromatic ring), such as might be required to accommodate the four coplanar substituents in these conformations, have been observed in total crystal structure determinations on related molecules.[17]

Steric Enhancement of Resonance. N-Alkylation, where steric factors play no part, causes reasonably constant red shifts of maxima arising from *para* amine → nitro interactions in nitroanilines, dinitroanilines, and dinitrophenylenediamines. In going from 4-nitroaniline ($\nu_{\max}^{\mathrm{MeOH}}$ 26,950 $\mathrm{cm^{-1}}$) to its N-methyl, N-ethyl, and N-isopropyl derivatives, bathochromic displacements ($\Delta\nu_{\max}$) amount to -1050, -1050, and -1240 $\mathrm{cm^{-1}}$, respectively. For N-methyl- and N-ethyl-2,4-dinitroaniline,[18] shifts in band-1 positions relative to **1**[8] (Table I) are -1020 and -1020 $\mathrm{cm^{-1}}$. With **4** (Table I) as the reference compound, the corresponding $\Delta\nu_{\max}$ value for 1,3-bis(ethylamino)-4,6-dinitrobenzene (**18**) is -1150 $\mathrm{cm^{-1}}$.[18]

These displacements are attributable primarily to inductive effects, which lead to increased ground-state electron densities on amine nitrogens and correspondingly decreased energies required for promotion to the $[\mathrm{RH^+N{=}C(1) \rightarrow C(4){=}NO_2^-}]$ electronic excited states. From the results cited above, we take the "normal" or nonsteric effect of N-monoalkylation of compounds of the types considered here to be bathochromic by *ca.* -1100 $\mathrm{cm^{-1}}$ in methanol.[3,19,20]

In going from **3** to the bis(N-alkylamino) derivatives **10–12**, however, $\nu_{\max}^{\mathrm{band\ 1a}}$ and $\nu_{\max}^{\mathrm{band\ 1b}}$ undergo appreciably greater bathochromic shifts than can be ascribed solely to this "normal" effect of N-alkylation on maxima arising from $[\mathrm{RH^+N{=}C(1) \rightarrow C(4){=}NO_2^-}]$ electronic transitions. As with other closely related series of compounds,[2–4] we consider that the increased displacements ($-\Delta\Delta\nu_{\max}$) beyond the "normal" 1100 $\mathrm{cm^{-1}}$ value derive, in large part, from the "*steric enhancement of resonance*" phenomenon.[1]

Since, as has been mentioned, there is a strong tendency toward band coalescence with alkyl substitution, $\Delta\Delta\nu_{\max}$ values are not the same for both bands in **10–12**. For convenience in intercomparisons, we have therefore found it useful to generate a term $\nu_{\max}^{\mathrm{band\ 1}}$, the "weighted midpoint" between maxima for band 1a and band 1b, which we calculate from the equation

$$\nu_{\max}^{\mathrm{band\ 1}} = \frac{(\nu_{\max}^{\mathrm{band\ 1a}})(\epsilon_{\max}^{\mathrm{band\ 1a}}) + (\nu_{\max}^{\mathrm{band\ 1b}})(\epsilon_{\max}^{\mathrm{band\ 1b}})}{\epsilon_{\max}^{\mathrm{band\ 1a}} + \epsilon_{\max}^{\mathrm{band\ 1b}}}$$

This method of taking the "weighted midpoint," which is considered to represent the "center of gravity" of the two-band system or the most probable position of the hypothetical "unsplit" band-1 maximum, compensates for the fact that 1b is the dominant band-1 component in **3**, while the 1a bands have the higher $\epsilon_{\max}$ values in **10–12**.[21] Values of $\nu_{\max}^{\mathrm{band\ 1}}$, $\Delta\nu_{\max}^{\mathrm{band\ 1}}$, and $\Delta\Delta\nu_{\max}^{\mathrm{band\ 1}}$ for **10–12** relative to **3** are given in Table II.

Table II. Steric Enhancement of Resonance as Evidenced by Spectral Displacements for 1,3-Bis(alkylamino)-2,4,6-trinitrobenzenes

No.	Substituents	$\nu_{\max}^{\mathrm{band\ 1}}$, $\mathrm{cm^{-1}}$	$\Delta\nu_{\max}^{\mathrm{band\ 1}}$, $\mathrm{cm^{-1}}$	$\Delta\Delta\nu_{\max}^{\mathrm{band\ 1}}$, $\mathrm{cm^{-1}}$
3	H	33,270		
10	$\mathrm{CH_3}$	30,890	-2380	-1280
11	$\mathrm{C_2H_5}$	30,790	-2480	-1380
12	i-$\mathrm{C_3H_7}$	30,510	-2760	-1660

The nature of the *steric enhancement of resonance* phenomenon has been detailed in earlier papers;[2–4] a similar rationale applies here. A $+2120$ $\mathrm{cm^{-1}}$ hypsochromic shift with the addition of a 2-nitro substituent is observed on going from $\nu_{\max}^{\mathrm{band\ 1}}$ 31,150 $\mathrm{cm^{-1}}$ for 1,3-diamino-4,6-dinitrobenzene (**4**) to $\nu_{\max}^{\mathrm{band\ 1}}$ 33,270 $\mathrm{cm^{-1}}$ (the "weighted midpoint") for 1,3-diamino-2,4,6-trinitrobenzene (**3**).[22] This is readily explained on the basis that a coplanar 2-nitro substituent reduces ground-state electron densities on the amino nitrogens by inductive and mesomeric electron withdrawal, with a corresponding suppression of 1 → 4 and 3 → 6 amino → nitro resonance interactions. The energy required for promotion to the $[\mathrm{H_2^+N{=}C(1) \rightarrow C(4){=}NO_2^-}]$ electronic excited state thus becomes greater for **3** than for **4**.

The 2-nitro substituents, when forced from planarity by the N-alkyl groups in **10–12**, exert less electron withdrawal than in **3**, however, since here only the inductive (but not the mesomeric) mechanism applies. Ground-state electron densities on the amine nitrogens are correspondingly higher than in hypothetical totally coplanar **10–12**, and electronic transition energies are corre-

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[16] We may rule out such a possibility in **9** since, though hypochromic relative to **6–8**, the effects on band 1a and band 1b are hyperchromic relative to **3**. With **13**, the effects are hypochromic relative to **3** as well as **10–12**.

[17] 2,3,4,6-Tetranitroaniline, ref 7; compound **3**, ref 15; 1,3-dichloro-2,4,6-trinitrobenzene, J. R. Holden and C. Dickinson, *J. Phys. Chem.*, 71, 4129 (1967); tetryl, H. Cady, *Acta Cryst.*, 23, 601 (1967); N-nitro-N-trifluoroethylpicramide, J. R. Holden and C. Dickinson, *J. Phys. Chem.*, in press.

[18] In these cases, the N-alkyl groups are most probably disposed in *s-trans* conformations relative to the neighboring nitro substituents. No diminutions in band-2 intensities such as would suggest steric inhibition of $[\mathrm{RH^+N{=}C(1) \rightarrow C(4){=}NO_2^-}]$ resonance are observed.[3]

[19] See, however, footnote 9 of ref 3, in which is discussed the $+600$ to 700 $\mathrm{cm^{-1}}$ hypsochromic contribution of decreasing hydrogen bonding *to* solvent to this "normal" effect of N-monoalkylation which in the summation is bathochromic. In isooctane, where hydrogen bonding *to* solvent is excluded, the $\Delta\nu_{\max}$ from 4-nitroaniline to N-methyl-4-nitroaniline is -1700 $\mathrm{cm^{-1}}$.[20] In the ensuing discussion, the implicit assumption is that parallel hypsochromic contributions to over-all spectral effects should result on eliminating a site for internal amine → nitro hydrogen bonding, such as predominates in **3**, and on eliminating a site for amine → solvent hydrogen bonding, such as is important in 4-nitroaniline, **1**, and **4**. In company with others (cited in ref 20), we feel that realistic assessment of spectral effects of hydrogen bonding *to* solvent is possible, but quantitative evaluation of effects of internal hydrogen bonding on the spectra still eludes us. We judge that this necessary assumption of equivalent hydrogen-bonding effects may introduce uncertainties, possibly as high as ±400 to 500 $\mathrm{cm^{-1}}$, in the intercomparisons we make here.

[20] M. J. Kamlet, *Israel J. Chem.*, 1, 428 (1963).

[21] If arithmetic midpoints between the maxima were taken, $-\Delta\Delta\nu_{\max}$ values would be higher still by *ca.* 200 $\mathrm{cm^{-1}}$.

[22] It is worthy of comment that the latter value (300.5 mμ) differs by 3.5 mμ from the position predicted in the Discussion dealing with band assignments on the basis of a comparison of the effects of analogous substitution on related compounds.

spondingly lower. The $\Delta\Delta\nu_{\max}$ values in Table II derive primarily from these lessened electron-withdrawal effects by the 2-nitro substituents in **10–12** relative to **3**.

If, as in earlier instances,[2–4] we describe the effect of the coplanar 2-nitro substituent in **3** as "electronic suppression of 1 → 4 and 3 → 6 amine → nitro resonance interactions," the effects of the alkyl groups in forcing this nitro from coplanarity in **10–12** become "steric diminution of electronic suppression of resonance interaction" or, more succinctly, "*steric enhancement of resonance*." The necessary condition proposed earlier,[3] that steric enhancement in one molecular axis is accompanied by steric inhibition of resonance in another molecular axis, is met in the present instance, *i.e.*, enhancement in 1 → 4 *vs.* inhibition in 1 → 2, enhancement in 3 → 6 *vs.* inhibition in 3 → 2.

It is likely that the above represents only part of the picture and that factors other than the steric enhancement phenomenon also contribute to the $\Delta\Delta\nu_{\max}$ values for **10–12**. It was suggested earlier[2,3] that electron withdrawal by a 90°-twisted nitro group should be about half of that for a coplanar nitro (*i.e.*, σ_I/σ_{para} or 0.63/1.27) and, from the +2120 cm^{-1} hypsochromic effect of the coplanar 2-nitro in going from **4** to **3**, we would expect about −1060 cm^{-1} as the shift deriving from an uncomplicated steric enhancement effect, rather than the −1280 to −1660 cm^{-1} which is observed.

Further, a commonality of spectral effects on adding coplanar *o*-nitro substituents to related compounds, such as discussed above, would imply also a commonality of effects on twisting these nitro's from coplanarity. The $\Delta\Delta\nu_{\max}$ values in the present series show good agreement with $\Delta\Delta\nu_{\max}$ −1280 to −1550 cm^{-1} on twisting the 2-nitro from planarity in the N,N-dialkyl-2,4-dinitroanilines,[3] and fair agreement with $\Delta\Delta\nu_{\max}/2$ −1595 to −1935 cm^{-1} when both *o*-nitro groups are twisted from planarity in the N,N-dialkylpicramides.[4] Agreement is poor, however, with the −730 to −810 cm^{-1} values which are observed when a single *ortho* nitro is twisted from planarity in the N-monoalkylpicramides.[4]

Uncertainties in the assumptions regarding the spectral effects of intramolecular hydrogen bonding in the unalkylated reference compounds[19] may account for some of these differences in the $\Delta\Delta\nu_{\max}$ values. Other differences are more likely to result from strong molecular distortions such as we have suggested might be imposed on the molecules in conformations D and E in order to allow four substituents to remain coplanar with the ring. For example, $\epsilon_{\max}^{\text{band 2}}$ values for 1,3-bis(ethylamino)-2,4,6-trinitrobenzene (**11**) and 1,3-bis(ethylamino)-4,6-dinitrobenzene are exactly equal (Table I), suggesting that the 2-nitro substituent is already twisted a full 90° from planarity in **11**. It would hence be difficult to ascribe the difference in $\Delta\Delta\nu_{\max}$ between **11** and **12** to steric enhancement or, since the reference compound is the same, to differential hydrogen bonding. Here, however, changing bond distances and valence angles with increasing alkyl group bulk provide a ready rationale in the light of comments by Ingraham[23] regarding a slight bathochromic effect of molecular distortion in benzene derivatives (presumably because less favorable ground-state orbital overlap labilizes the π-electron system toward electronic excitation).

Electronic Buttressing. It has been suggested that amine → nitro mesomerism "stiffens" both the amine and the nitro groups against being twisted from coplanarity by bulky neighbors; the effect has been termed "electronic buttressing."[3,5] Our *a priori* preference for conformation C or D over B for compounds **6–8** had been based on the premise that fewer such interactions would be excluded and the consequent sacrifice in resonance stabilization would be less if a single nitro rather than a single amine were rotated from planarity (*i.e.*, 1 → 6, 3 → 6 in C or 1 → 2, 3 → 2 in D *vs.* 1 → 2, 1 → 4, 1 → 6 in B).

In the choice between conformations C and D, the dominant question was whether a greater over-all loss in free energy ensued with the exclusion of two *ortho* interactions and an intramolecular (3 → 2) hydrogen bond in D, or with the exclusion of a single *ortho* and a *para* interaction in C. That D proved to be the preferred conformation for **6–8** is consistent with observations described earlier, wherein exactly analogous considerations regarding relative stabilization by *ortho* and *para* amine → nitro mesomerism applied.[5–7] It was shown there that the 3 substituent in 2,3,4,6-tetranitroaniline imposed greater rotation from planarity on the 2- than on the 4-nitro group. Similarly, the aminopicryl groups in 3,3′-diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl forced greater angles of twist on the 2- and 2′- than on the 6- and 6′-nitro substituents.

Taken together, these findings from the spectra–structure studies (confirmed in one instance by the total crystal structure determination)[7] provide strong evidence that [$\text{RH}^+\text{N}{=}\text{C}(1) \rightarrow \text{C}(4){=}\text{NO}_2^-$] mesomerism contributes significantly more than [$\text{RH}^+\text{N}{=}\text{C}(1) \rightarrow \text{C}(2){=}\text{NO}_2^-$] mesomerism to over-all resonance stabilization of nitro- and polynitroanilines.[24]

Going from conformation D for **6–8** to conformation E for **10–12** necessitates no further sacrifice in mesomeric stabilization. Here, both *ortho* and *para* amine → nitro interactions buttress each coplanar substituent, whereas any of the possible alternative conformations would necessarily involve sacrificing one or both of the *para* interactions.

1-Dialkylamino-3-amino- and 1,3-Bis(dialkylamino)-2,4,6-trinitrobenzenes. Steric effects on the spectra of the N,N-dialkyl derivatives of **3** (Figure 5) extend some but reverse other of the trends observed earlier. As before, band-1a and band-1b maxima for 1-(dimethylamino)-3-amino- (**14**) and 1-(diethylamino)-3-amino-2,4,6-trinitrobenzene (**15**) show significant bathochromic shifts relative to the corresponding monoalkyl derivatives, **6** and **7**, while band-2 positions remain relatively unaffected. Here, however, the effects on absorption intensities are strongly *hypo*chromic for all three bands, substitution by the second N-alkyl group causing the following decreases: for **14** relative to **6**, $\Delta\epsilon_{\max}^{\text{band 1a}}$ −34.6%, $\Delta\epsilon_{\max}^{\text{band 1b}}$ −24.9%, $\Delta\epsilon_{\max}^{\text{band 2}}$ −21.4%; for **15** relative to **7**, $\Delta\epsilon_{\max}^{\text{band 1a}}$ −41.8%, $\Delta\epsilon_{\max}^{\text{band 1b}}$ −31.1%, $\Delta\epsilon_{\max}^{\text{band 2}}$ −25.0%.

Further, despite marked band broadening with correspondingly increased band overlap,[25] the tendency

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[23] L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 500.

[24] A lower limit to the magnitude of the increased contribution of the *para* relative to the *ortho* interactions would be in the strength of the hydrogen bond which is sacrificed as the *o*-nitro is twisted from planarity minus the strength of the hydrogen bond *to* solvent which is formed.

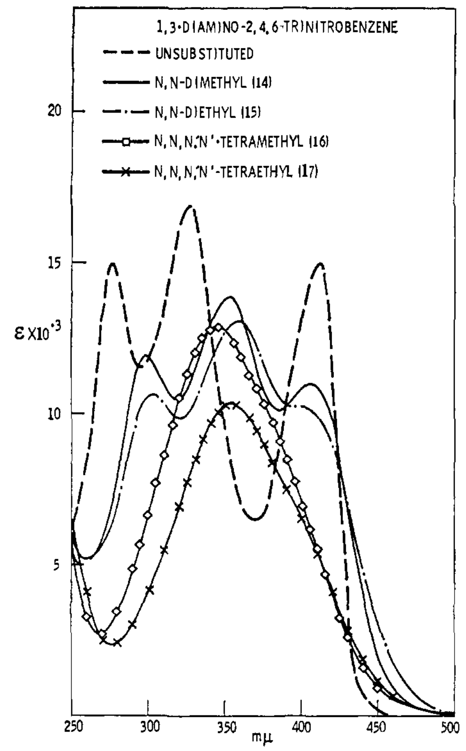

Figure 5. Absorption spectra of the N,N-dialkyl and N,N,N',N'-tetraalkyl derivatives of 1,3-diamino-2,4,6-trinitrobenzene.

toward band coalescence, which was observed in going from **3** to **6–8**, is reversed in going to **14** and **15**. Values of $\nu_{\max}^{1a} - \nu_{\max}^{1b}$ are: for **14**, 5070 cm^{-1}; for **15**, 5180 cm^{-1}.

Although these effects on the spectra, taken together, allow no unequivocal choice of preferred conformations for the N,N-dialkyl derivatives, certain of the various possibilities may be deemed to be more or less likely. We may exclude conformations like D, for example, inasmuch as the reduced absorption intensities of the band-1 components in **14** and **15** relative to **6** and **7** would require that at least one substituent, which had been coplanar in the earlier instances, now be rotated strongly from planarity. Although possibilities involving 90°-twisted 1-dialkylamine groups and essentially coplanar 2, 3, 4, and 6 substituents could account for the reduced intensities, they also seem less likely on the basis that they would be expected to lead to stronger band coalescence than is observed, with a trend toward resembling more closely the spectrum of **2**.

On balance, we consider that the spectra of **14** and **15** are most readily rationalized in terms of conformations wherein the 1-alkylamino and 2-nitro substituents are subjected to partial in-phase rotations (but with sufficient residual p–π or π–π overlap that their contributions to the spectra remain significant, *i.e.*, angles of twist θ = 30–50°) and with a somewhat lesser in-phase angle of twist imposed on the 6-nitro substituents. Such conformations, wherein both the *ortho* and the *para* amine → nitro electronic transitions would be subject to roughly similar effects of steric inhibition of resonance,[26] are consistent with the appreciably lesser band coalescence than in **6–9** or **10–13** and the comparable reductions in all $\epsilon_{\max}$ values relative to **3**.[27]

In these preferred conformations, the conditions around the 1 position in **14** and **15** resemble that around the 3 position in 2,3,4,6-tetranitroaniline. It therefore deserves comment that, if we had taken known angles of twist in the latter compound as points of reference, *a priori* estimates of θ values for **14** and **15** might not have differed markedly from those deduced from the spectra. For example, strong electronic buttressing by the 4 substituents in **14** and **15** could be expected to outweigh the increased spatial requirements of dialkylamine relative to nitro. Hence, $\theta_{1\text{-R}_2\text{N}}$ should be somewhat (but not excessively) smaller than 64°, the observed value for $\theta_{3\text{-NO}_2}$ in the crystal of tetranitroaniline;[7] $\theta_{1\text{-R}_2\text{N}}$ = 30–50° seems highly reasonable on this basis. Further, $\theta_{2\text{-NO}_2}$ and $\theta_{6\text{-NO}_2}$ in **14** and **15** should not differ markedly from the 42–45° and 19–21° values observed in the crystal and deduced from the spectra for the corresponding nitro substituents (2 and 4) in tetranitroaniline.[5–7] The basis for the latter conclusion would be that, in assessing relative effects of 30–50°-twisted dialkylamine and 64°-twisted nitro neighbors on nitro group coplanarity, steric and mesomeric factors (weaker here than those buttressing the 1 substituent) should tend to offset one another.

Also shown in Figure 5 are 1,3-bis(dimethylamino)- (**16**) and 1,3-bis(diethylamino)-2,4,6-trinitrobenzene (**17**). In these N,N,N',N'-tetraalkyl derivatives of **3**, the characteristic three-peak spectra have fused to single broad bands with only weak inflections on the longer wavelength edges to mark contributions by the submerged components. Total integrated absorption intensities (IAI)[28] for **16** and **17** are 61 and 47%, respectively, of the IAI for **3** and might properly be lower if the normal hyperchromic effect of N-alkylation were taken into account and the comparison were with hypothetical totally coplanar **16** and **17**.

These spectra suggest that all substituents in **16** and **17** are rotated strongly from coplanarity. As with analogous highly hindered compounds (*e.g.*, 2,3,4,5,6-pentanitroaniline),[5] we prefer propeller-like conformations; in-phase angles of twist here might be in the order of 50–70°.

It is worth mentioning in conclusion that individual deductions of molecular conformations from absorption spectra, such as have here occupied our attention, need no longer stand by themselves. They are supported and in turn support a body of information which has now been assembled for a large number of related compounds.[2–7] Thus, they become part of a generalized self-consistent framework for predicting effects of systematic substituent variation on the shapes taken by organic molecules in the aminonitroaromatic series.

Experimental Section

Spectra. Absorption spectra were determined in methanol (containing in some cases <1% tetrahydrofuran) using a Cary Model 14 recording spectrophotometer with matched 1-cm silica cells. Concentrations were 3–10 × 10^{-5} *M*. Previously described precau-

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[25] Band broadening often accompanies steric inhibition of resonance; but here it may also be due, in large part, to increasing nonequivalence of the 1 → 4 dialkylamino → nitro and the 3 → 6 amino → nitro electronic transitions.

[26] In **14** and **15**, we encounter a situation where the same bands appear simultaneously to be influenced by both steric inhibition and steric enhancement of resonance. The former operates by reducing $\epsilon_{\max}$; the latter accounts in large part for the bathochromic shifts of $\lambda\lambda_{\max}$.

[27] The dissimilar reductions in $\epsilon_{\max}$ values noted earlier were relative to **6** and **7**, rather than to **3**.

[28] The IAI is the $\epsilon d\nu$ integral for the total spectral envelope taken from the minimum on the blue side of band 1a.

tions[29] were taken to guard against photochemical transformations.

1,3-Diamino-2,4,6-trinitrobenzene Derivatives. Procedures reported by Forster and Coulson[30] were used in the preparation of the N-methyl derivative **6**, mp 190–192° (lit.[30] 190°), and the N,N-dimethyl derivative **14**, mp 183–184° (lit.[30] 187°).

Anal. Calcd for $C_8H_9N_5O_6$ (**14**): C, 35.43; H, 3.34; N, 25.83; mol wt, 271. Found: C, 35.52; H, 3.50; N, 25.70; mol wt, 275.

The N-ethyl derivative **7** was prepared by adding 1.4 g of 2,3,4,6-tetranitroaniline to 10 ml of cold 70% aqueous ethylamine, stirring for 0.5 hr, and warming to ambient temperature. After pouring the deep red solution into 100 ml of water, 1:1 aqueous hydrochloric acid was added until the mixture was acidic, then solid potassium carbonate until slightly basic. The solid was filtered, washed, and recrystallized from methanol to give **7** in the form of deep amber crystals, mp 161–163°.

Anal. Calcd for $C_8H_9N_5O_6$: C, 35.43; H, 3.34; N, 25.83; mol wt, 271. Found: C, 35.62; H, 3.56; N, 25.92; mol wt, 274.

For the preparation of the N-isopropyl derivative **8**, 1.4 g of 2,3,4,6-tetranitroaniline was suspended in 25 ml of methanol and 4 ml of isopropylamine was added. Gentle boiling for 2 hr gave an orange precipitate which was filtered and washed with a small amount of methanol. Recrystallization from acetone–methanol gave pure **8** as orange needles, mp 136–137°.

Anal. Calcd for $C_9H_{11}N_5O_6$: C, 37.90; H, 3.89; N, 24.56; mol wt, 285. Found: C, 38.15; H, 4.20; N, 24.40; mol wt, 289.

The preparation of the N-*t*-butyl derivative **9** was similar to that of **8**, except that 3-methoxy-2,4,6-trinitroaniline and *t*-butylamine were the starting materials. The product was obtained in the form of bright yellow crystals, mp 174–175°.

Anal. Calcd for $C_{10}H_{13}N_5O_6$: C, 40.13; H, 4.38; N, 23.41, mol wt, 299. Found: C, 40.00; H, 4.63; N, 23.22; mol wt, 302.

A literature method for the preparation of the N,N′-dimethyl derivative **10**[31] gave, in our hands, an impure product. A preferred procedure involved bubbling methylamine into a solution of 3.7 g of 1,3-dibromo-2,4,6-trinitrobenzene in 50 ml of benzene at room temperature. After filtering the solid and washing with benzene, it was stirred with a mixture of 95 ml of water and 5 ml of concentrated hydrochloric acid. Recrystallization from acetone–tetrahydrofuran yielded **10** as small yellow needles, mp 235–238° dec (lit.[31] 235–240° dec).

The procedure for the N,N′-diethyl derivative **11** was similar to that used for **7**, except that 1,3-dimethoxy-2,4,6-trinitrobenzene was treated with the 70% aqueous ethylamine. The product was obtained as bright yellow needles, mp 143–144° (lit.[32] 144°).

The N,N′-diisopropyl derivative **12** was prepared by suspending 2.7 g of 1,3-dimethoxy-2,4,6-trinitrobenzene in 50 ml of methanol and adding 20 ml of isopropylamine. The amber solution was stirred 0.5 hr and poured into 300 ml of water; 1:1 aqueous hydrochloric acid was added until the mixture was only slightly basic and a massive yellow precipitate had formed. Filtering the solid, washing with water, and recrystallizing from methanol gave pure **12** as bright yellow needles, mp 143–144°.

Anal. Calcd for $C_{12}H_{17}N_5O_6$: C, 44.03; H, 5.24; N, 21.40; mol wt, 327. Found: C, 44.12; H, 5.39; N, 22.22; mol wt, 327.

The preparation of the N,N′-di-*t*-butyl derivative **13** was essentially the same as that of **12** except that *t*-butylamine was the reagent. Recrystallization from aqueous methanol gave bright yellow crystals, mp 137–138°.

Anal. Calcd for $C_{14}H_{21}N_5O_6$: C, 47.32; H, 5.96; N, 19.71; mol wt, 355. Found: C, 47.40; H, 6.06; N, 19.97; mol wt, 355.

To prepare the N,N-diethyl derivative **15**, the method of Forster and Coulson[30] for the corresponding dimethyl derivative was modified by the use of methanol as solvent and diethylamine as the reactant with 2,3,4,6-tetranitroaniline. The product was recrystallized from acetone–methanol to give **15** as orange crystals, mp 150–151°.

Anal. Calcd for $C_{10}H_{13}N_5O_6$: C, 40.13; H, 4.38; N, 23.41; mol wt, 299. Found: C, 40.13; H, 4.61; N, 22.97; mol wt, 302.

The N,N,N′,N′-tetramethyl derivative **16** was prepared by adding 10 g of dimethylamine to 3.7 g of 1,3-dibromo-2,4,6-trinitrobenzene in 50 ml of benzene at ice-bath temperature. The solid was filtered, washed with benzene, and stirred with water. Dilute hydrochloric acid was added to the aqueous suspension until only slightly basic and a yellow precipitate had formed. The product was filtered, washed with water, and purified by pouring an acetone solution into water to give **16** in the form of yellow platelets, mp 142–143°.

Anal. Calcd for $C_{10}H_{13}N_5O_6$: C, 40.13; H, 4.38; N, 23.41; mol wt, 299. Found: C, 40.17; H, 4.66; N, 22.93; mol wt, 298.

For the preparation of the N,N,N′,N′-tetraethyl derivative **17**, 15 ml of diethylamine was added to 3.7 g of 1,3-dibromo-2,4,6-trinitrobenzene in the cold. After standing overnight at room temperature, methanol was added and hydrogen chloride gas was passed in until very acidic. All volatiles were removed with a rotary evaporator and the solid residue was taken up in acetone and poured into water. The precipitate was filtered, washed with water, and recrystallized from methanol to give **17** as yellow-orange crystals, mp 116–117.5°

Anal. Calcd for $C_{14}H_{21}N_5O_6$: C, 47.32; H, 5.96; N, 19.71; mol wt, 355. Found: C, 47.27; H, 6.27; N, 19.92; mol wt, 352.

The method of Mustafa and Zahran[33] was used for the preparation of 1,3-bis(ethylamino)-4,6-dinitrobenzene (**18**), mp 176° (lit.[33] 173.5°).

Melting points are uncorrected. Molecular weights by the osmometric method were by Mr. D. J. Glover of this laboratory. Elemental analyses were by Dr. Mary H. Aldridge, Department of Chemistry, The American University, Washington, D. C.

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