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Enthalpies of combustion of 2,2′,6,6′-tetraethylazobenzene *N*,*N*-dioxide, 2,4,6-tri(1,1-dimethylethyl)nitrosobenzene, and 2,4,6-tri(1,1-dimethylethyl)nitrobenzene

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The standard ($p^\circ = 0.1\,\text{MPa}$) molar enthalpies of combustion at the temperature $T = 298.15\,\text{K}$ were measured by static-bomb calorimetry for crystalline 2,2′6,6′-tetraethylazobenzene *N*,*N*-dioxide, $\{2,6\text{-}(C_2H_5)_2C_6H_3N(O)\cdot\}_2$; 2,4,6-tri(1,1-dimethylethyl)nitrosobenzene, $2,4,6\text{-}\{CH_3C(CH_3)_2\}_3C_6H_2NO$; and 2,4,6-tri(1,1-dimethylethyl)nitrobenzene, $2,4,6\text{-}\{CH_3C(CH_3)_2\}_3C_6H_2NO_2$. The standard molar enthalpies of sublimation at $T = 298.15\,\text{K}$ of the tri(1,1-dimethylethyl) compounds were measured by microcalorimetry.

	$-\Delta_c H_m^\circ(\text{cr})/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta_{\text{cr}}^{\text{g}} H_m^\circ/(\text{kJ}\cdot\text{mol}^{-1})$
$\{2,6\text{-}(C_2H_5)_2C_6H_3N(O)\cdot\}_2$	11585.5 ± 2.6	—
$2,4,6\text{-}\{CH_3C(CH_3)_2\}_3C_6H_2NO$	11019.3 ± 3.7	91.0 ± 3.2
$2,4,6\text{-}\{CH_3C(CH_3)_2\}_3C_6H_2NO_2$	10956.4 ± 3.2	81.4 ± 1.8

The standard molar enthalpy of decomposition of $\{2,6\text{-}(C_2H_5)_2C_6H_3N(O)\cdot\}_2$ to form $2,6\text{-}(C_2H_5)_2C_6H_3NO(g)$ at $T = 298.15\,\text{K}$ was measured by microcalorimetry: $\Delta_{\text{dec}} H_m^\circ/(\text{kJ}\cdot\text{mol}^{-1}) = (200.6 \pm 5.6)$. Application of group-additivity schemes applied to nitrosobenzene and nitrobenzene derivatives shows that 2,4,6-tri(1,1-dimethylethyl)nitrosobenzene is unstrained whereas the corresponding nitrocompound shows considerable strain in accord with an X-ray structure analysis demonstrating that steric hindrance prevents dimerization of the nitrosoderivative. © 1995 Academic Press Limited

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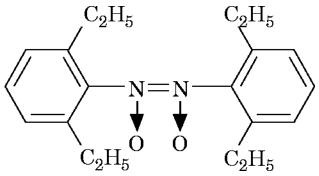
1. Introduction

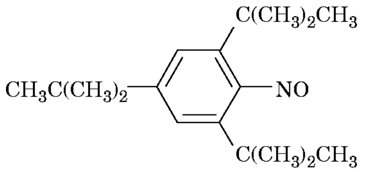
Crystalline aromatic *C*-nitroso compounds can be either white or green: when white the compounds are dimeric and when green, monomeric. Crystal-structure determinations of nitrosobenzene,(1) 4-bromonitrosobenzene,(2) and 2,4,6-tribromonitrosobenzene,(3) show these white compounds to be dimeric whereas for 4-iodonitrosobenzene,(4) and 4-dimethylaminonitrosobenzene,(5) they show these green compounds to be monomeric. Previous thermochemical studies showed that substitution of the electron-donating dimethylamino group *para* to the nitroso group results in exceptional stabilization of the monomer, making formation of the dimer energetically unfavourable.(6)

The white dimeric forms melt to give green liquids and the vapour at high temperatures and low pressures will decompose to the monomer, thus previous thermochemcial measurements on 2,2′,4,4′,6,6′-hexamethylazobenzene *N*,*N*-dioxide and 2,2′,6,6′-tetramethylazobenzene *N*,*N*-dioxide led to values for the enthalpies of formation of 2,4,6-trimethylnitrosobenzene and of 2,6-dimethylnitrosobenzene in the gaseous state.(7) It is to be expected that increasing the size of the groups *ortho* to the nitroso group would eventually result in prevention of dimerization.

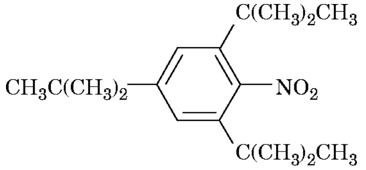
In this paper we report the enthalpy of combustion of 2,2′,6,6′-tetraethylazobenzene *N*,*N*-dioxide:



a white crystalline solid, and the enthalpy of its decomposition to the gaseous monomer: also the enthalpies of combustion of 2,4,6-tri(1,1-dimethylethyl)nitrosobenzene:



and of 2,4,6-tri(1,1-dimethylethylnitrobenzene:



together with the enthalpies of sublimation, to investigate whether the green monomeric nitroso compound fails to dimerize due to stabilization of the monomer or due to steric hindrance in formation of the dimer.

2. Experimental

2,2′,6,6′-tetraethylazobenzene *N*,*N*-dioxide was prepared by oxidation of 2,6-diethylaniline using sodium tungstate plus hydrogen peroxide as described by Stowell and Lau,(8) and purified by four crystallizations from (benzene + hexane). 2,4,6-Tri(1,1-dimethylethyl)nitrosobenzene was prepared by oxidation of 2,4,6-tri(1,1-dimethylethyl)aniline with two equivalents of peroxybenzoic acid in dichloromethane at the temperature 273 K,(9, 10) and purified by sublimation *in vacuo*. 2,4,6-Tri(1,1-dimethylethyl)nitrobenzene (Aldrich) was recrystallized four times from methanol. Elemental analyses were in agreement with expected values: mass fractions for $C_{20}H_{26}N_2O_2$: found: C, 0.7344; H, 0.0807; N, 0.0863; calculated: C, 0.7359; H, 0.0803; N, 0.0858, for $C_{18}H_{29}NO$: found: C, 0.7841; H, 0.1055; N, 0.0516; calculated: C, 0.7849; H, 0.1061; N, 0.0509, and for $C_{18}H_{29}NO_2$; found: C, 0.7431; H, 0.0998; N, 0.0472; C, 0.7418; H, 0.1003; N, 0.0481. The densities of the samples and the average ratios of the mass of carbon dioxide produced by the sample to that calculated from its mass with uncertainties of twice the standard deviation of the mean were: $C_{20}H_{26}N_2O_2$: $\rho/(\mathrm{g\cdot cm^{-3}}) = 1.35$, (1.0000 ± 0.0001); $C_{18}H_{29}NO_2$: $\rho/(\mathrm{g\cdot cm^{-3}}) = 0.85$ (estimated), (0.9998 ± 0.0001); $C_{18}H_{29}NO_2$: $\rho/(\mathrm{g\cdot cm^{-3}}) = 0.85$ (estimated), (1.0001 ± 0.0004).

Hexadecane (Aldrich, Gold Label) stored under nitrogen was used in some experiments as an auxiliary combustion aid.

2,4,6-Tri(1,1-dimethylethyl)nitrobenzene was further characterized by X-ray crystallography using an Enraf-Nonius CAD-4 diffractometer.(11) The results showed that this molecule crystallizes in the hexagonal space group P$\bar{6}$2c, but with a considerable degree of disorder. Due to this disorder, a refined model for the structure could not be derived but sufficient information was obtained to render some clarification of the overall structure. The disorder was characterized as both intramolecular and intermolecular. The benzene ring lies on a mirror plane ($z = 1/4$), perpendicular to a six-fold inversion axis (1/3, 2/3, 1/4). Every carbon position therefore, is bonded to a 1/6 occupancy nitro group and a 1/2 occupancy 1,1-dimethylethyl moiety. Within the resolution of the model, the nitrogen and the quaternary carbon atoms coincide. Six points of electron density connect to this coincident point, corresponding to two coincident C/O "atoms" and four 1/4 occupancy carbons, all of which lie out of the aromatic plane. Thus the nitro group adopts an orientation perpendicular to the benzene ring, and the 1,1-dimethylethyl groups adopt one of two orientations that place the carbons at dihedral angles of $-\pi/6$, $\pi/2$, and $-5\cdot\pi/6$ with respect to the ring. The intermolecular disorder consists of each O/C position lying on a three-fold axis (2/3, 1/3, z; and 0, 0, z). The overall structure, therefore, consists of numerous peaks of partial and/or mixed occupancies. Germane to this discussion, however, is the fact that all peaks could be located through both direct and Fourier-difference methods (if not refined), and none of the attached group peaks lies in the same plane as the aromatic ring.

The enthalpy of combustion of 2,2′,6,6′-tetraethylazobenzene *N*,*N*-dioxide was measured using the Manchester static-bomb calorimeter,(12, 13) whereas 2,4,6-tri(1,1-dimethylethyl)nitrosobenzene and 2,4,6-tri(1,1-dimethylethyl)nitrobenzene were measured using the Porto static-bomb calorimeter.(14, 15) The energy equivalent of the Manchester bomb calorimeter was determined from the combustion of benzoic acid (NBS SRM 39i) having a massic energy of combustion under standard bomb conditions of $(26434 \pm 3)\ \mathrm{J{\cdot}g^{-1}}$. From 12 calibration experiments, $\varepsilon(\mathrm{calor}) = (15525.40 \pm 0.47)\ \mathrm{J{\cdot}K^{-1}}$ where the uncertainty quoted is the standard deviation of the mean for an average mass of water added to this calorimeter of 2897.0 g. The Porto bomb calorimeter was calibrated using benzoic acid (Bureau of Analysed Samples, CRM 190p) having a massic energy of combustion under standard bomb conditions of $(26431.8 \pm 3.7)\ \mathrm{J{\cdot}g^{-1}}$. From nine calibration experiments, $\varepsilon(\mathrm{calor}) = (15911.2 \pm 1.5)\ \mathrm{J{\cdot}K^{-1}}$ for an average mass of water added to this calorimeter of 3119.6 g.

The experimental conditions were similar for both calorimeters. Samples, in pellet form, were ignited at $T = (298.150 \pm 0.001)$ K in oxygen at a pressure $p = 3.04$ MPa with a volume 1 $\mathrm{cm^3}$ of water added to the bomb. The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $-\Delta_c u^\circ = 16250\ \mathrm{J{\cdot}g^{-1}}$.(16) For the combustion auxiliary aid, hexadecane, from separate measurements, $-\Delta_c u^\circ = (47156.9 \pm 1.2)\ \mathrm{J{\cdot}g^{-1}}$. Corrections for nitric-acid formation were based on $-59.7\ \mathrm{kJ{\cdot}mol^{-1}}$ for the molar energy of formation of 0.1 $\mathrm{mol{\cdot}dm^{-3}}$ HNO_3(aq) from N_2, O_2, and H_2O(l).(17) The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton-thread fuse and hexadecane. For each compound $(\partial u/\partial p)_T$ at $T = 298.15$ K was assumed to be $-0.2\ \mathrm{J{\cdot}g^{-1}{\cdot}MPa^{-1}}$, a value typical for most organic solids. For each compound, $\Delta_c u^\circ$ was calculated by the procedure given by Hubbard *et al.*(16) The molar masses used for the elements were those recommended by the IUPAC Commission.(18)

The standard molar enthalpies of sublimation of 2,4,6-$\{CH_3C(CH_3)_2\}_3C_6H_2NO$ and 2,4,6-$\{CH_3C(CH_3)_2\}_3C_6H_2NO_2$ and the enthalpy of decomposition of $\{2,6\text{-}(C_2H_5)_2C_6H_3N(O)\cdot\}_2$ were measured by the "vacuum sublimation" drop-microcalorimetric method.(19) Samples (of mass about 5 mg) of each compound

TABLE 1. Typical combustion results ($p^\circ = 0.1$ MPa)

	$\{2,6\text{-}(C_2H_5)_2C_6H_3N(O)\cdot\}_2$	2,4,6-$\{CH_3C(CH_3)_2\}_3C_6H_2NO$	2,4,6-$\{CH_2C(CH_3)_2\}_3C_6H_2NO_2$
$m(CO_2,\mathrm{total})/\mathrm{g}$	2.75718	1.79155	1.69334
$m(\mathrm{cpd})/\mathrm{g}$	1.02087	0.62118	0.32944
$m(\mathrm{hexadecane})/\mathrm{g}$	—	—	0.25473
$m(\mathrm{fuse})/\mathrm{g}$	0.00281	0.00306	0.00355
$\Delta T_{ad}/\mathrm{K}$	2.33701	1.56401	1.53647
$\varepsilon_f/(\mathrm{J{\cdot}K^{-1}})$	14.8	16.5	16.6
$\Delta m(H_2O)/\mathrm{g}$	0.0	-0.4	-0.4
$-\Delta U(\mathrm{IBP})/\mathrm{J}$	36316.5	24907.4	24469.0
$\Delta U(HNO_3)/\mathrm{J}$	59.0	28.1	26.6
$\Delta U(\mathrm{ign})/\mathrm{J}$	1.1	1.1	1.0
$\Delta U_\Sigma/\mathrm{J}$	18.6	10.1	8.3
$-m\Delta_c u^\circ(\mathrm{hexadecane})/\mathrm{J}$	—	—	12012.1
$-m\Delta_c u^\circ(\mathrm{fuse})/\mathrm{J}$	45.6	49.7	57.7
$-\Delta_c u^\circ(\mathrm{cpd})/(\mathrm{J{\cdot}g^{-1}})$	35453.4	39955.4	37531.3

contained in a small thin glass capillary tube sealed at one end were dropped at room temperature into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter and then removed from the hot zone by vacuum sublimation. The observed standard molar enthalpies of sublimation $\{H^\circ_m(\mathrm{g}, T) - H^\circ_m(\mathrm{cr}, 298.15\ \mathrm{K}\}$ were corrected to $T = 298.15$ K using $\Delta^T_{298.15\ \mathrm{K}} H^\circ_m(\mathrm{g})$ estimated by a group method based on the values of Stull *et al.*(20) The observed enthalpy of decomposition of $\{2,6\text{-}(C_2H_5)_2C_6H_3N(O)\cdot\}_2(\mathrm{cr})$, $\{2H^\circ_m(\mathrm{monomer, g}, T) - H^\circ_m(\mathrm{cr, dimer}, 298.15\ \mathrm{K})\}$, was corrected to $T = 298.15$ K in a similar fashion. For this decomposition, the calorimeter was held at a sufficiently high temperature and this temperature was varied to ensure that the decomposition was complete. The microcalorimeter was calibrated *in situ* by making use of the reported molar enthalpy of sublimation of naphthalene, $C_{10}H_8$: $(72.51 \pm 0.01)\ \mathrm{kJ \cdot mol^{-1}}$.(21)

3. Results

Results for a typical combustion experiment on each compound are given in table 1: $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from the mass assigned for ε(calor); ΔU_Σ is the correction to the standard state; the remaining terms are as previously described.(16) As samples were ignited at $T = (298.150 \pm 0.001)$ K: $\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + c_p(H_2O, \mathrm{l}) \cdot \Delta m(H_2O) + \varepsilon_f\}\Delta T_{ad} + \Delta U(\mathrm{ign})$; where ΔT_{ad} is the calorimeter temperature change corrected for heat exchange and the work of stirring. The individual values of $-\Delta_c u^\circ$ together with the mean and its standard deviation are given in table 2. Table 3 lists the derived standard molar enthalpies of combustion and of formation in the condensed and gaseous states. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion and formation are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the auxiliary quantities used. To derive $\Delta_f H^\circ_m$ from $\Delta_c H^\circ_m$ the standard molar enthalpies of formation: for H_2O(l): $-(285.83 \pm 0.04)\ \mathrm{kJ \cdot mol^{-1}}$ and for CO_2(g): $-(393.51 \pm 0.13)\ \mathrm{kJ \cdot mol^{-1}}$ were used.(22)

TABLE 2. Values of $-\Delta_c u^\circ$ at $T = 298.15$ K ($p^\circ = 0.1$ MPa)

$\{2,6\text{-}(C_2H_5)_2C_6H_3N(O)\cdot\}_2$	$2,4,6\text{-}\{CH_3C(CH_3)_2\}_3C_6H_2NO$	$2,4,6\text{-}\{CH_3C(CH_3)_2\}_3C_6H_2NO_2$	
	$-\Delta_c u^\circ/(\mathrm{J \cdot g^{-1}})$		
35456.9	39939.4	37558.1	37548.2
35443.7	39963.5	37551.9	37546.4
35453.4	39937.3	37538.7	37531.3
35455.3	39944.2	37556.3	
35465.7	39965.2	37544.9	
35463.9	39955.4	37536.1	
	$-\langle\Delta_c u^\circ\rangle/(\mathrm{J \cdot g^{-1}})$		
35456.5 ± 3.2	39950.8 ± 5.0		37545.8 ± 3.0

TABLE 3. Derived standard molar values at $T = 298.15$ K ($p^\circ = 0.1$ MPa)

	$\frac{-\Delta_c U_m^\circ(\mathrm{cr})}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{-\Delta_c H_m^\circ(\mathrm{cr})}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{\Delta_f H_m^\circ(\mathrm{cr})}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\circ}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{\Delta_f H_m^\circ(\mathrm{cr})}{\mathrm{kJ \cdot mol^{-1}}}$
$\{2,6\text{-}(C_2H_5)_2C_6H_3N(O)\cdot\}_2$	11574.3 ± 2.6	11585.5 ± 2.6	-0.5 ± 3.8	200.6 ± 5.6 [a]	
$2,4,6\text{-}\{CH_3C(CH_3)_2\}_3C_6H_2NO$	11003.8 ± 3.7	11019.3 ± 3.7	-208.4 ± 4.4	91.0 ± 3.2	-117.4 ± 5.4
$2,4,6\text{-}\{CH_3C(CH_3)_2\}_3C_6H_2NO_2$	10942.1 ± 3.2	10956.4 ± 3.2	-271.3 ± 4.0	81.4 ± 1.8	-189.9 ± 4.4

[a] Corresponds to dimer(cr) = 2·monomer(g).

4. Discussion

From the molar enthalpies of formation and decomposition of $\{2,6\text{-}(C_2H_5)_2C_6H_3N(O)\cdot\}_2$: $\Delta_f H_m^\circ\{2,6\text{-}(C_2H_5)_2C_6H_3NO, g\} = (100.1 \pm 3.4)\ \mathrm{kJ \cdot mol^{-1}}$ is derived. In table 4, the observed $\Delta_f H_m^\circ(g)$ values for C_6H_5NO derivatives are compared with those calculated using the Cox scheme,(23) in which each group is associated with a characteristic increment in $\Delta_f H_m^\circ(g)$ when substituted into the benzene ring. Cox proposed corrections for steric hindrance between neighbouring groups but no such corrections have been made here. To derive the calculated values, an average increment for substitution of the NO group into C_6H_6 of $(122.4 \pm 2.2)\ \mathrm{kJ \cdot mol^{-1}}$ was used together with the following values of $\Delta_f H_m^\circ(g)/(\mathrm{kJ \cdot mol^{-1}})$: C_6H_6, (82.6 ± 0.7);(24) $1,3\text{-}(CH_3)_2C_6H_4$, (17.3 ± 0.8);(24) $1,3,5\text{-}(CH_3)_3C_6H_3$, $-(15.9 \pm 1.3)$;(24) $1,3\text{-}(C_2H_5)_2C_6H_4$, $-(21.8 \pm [2.5])$;(25) $C_6H_5N(CH_3)_2$, (100.5 ± 4.7).(24) $\Delta_f H_m^\circ(g)/(\mathrm{kJ \cdot mol^{-1}})$ for $CH_3C(CH_3)_2C_6H_5$: $-(22.6 \pm 1.2)$,(24) was used to estimate $\Delta_f H_m^\circ(g)/(\mathrm{kJ \cdot mol^{-1}})$ of $1,3,5\text{-}\{CH_3C(CH_3)_2\}_3C_6H_3$: $-(233.0 \pm 3.7)$. From the comparison in table 4 it is clear

TABLE 4. Observed and calculated $\Delta_f H_m^\circ(g)$ values for nitrosobenzene derivatives

	$\Delta_f H_m^\circ(g)/(\mathrm{kJ \cdot mol^{-1}})$ observed	$\Delta_f H_m^\circ(g)/(\mathrm{kJ \cdot mol^{-1}})$ calculated	$\frac{\Delta\Delta_f H_m^\circ}{\mathrm{kJ \cdot mol^{-1}}}$
C_6H_5NO	209.8 ± 8.0 (7)	205.0 ± 2.3	4.8 ± 8.3
$2,6\text{-}(CH_3)_2C_6H_3NO$	139.8 ± 1.6 (7)	139.7 ± 2.3	0.1 ± 2.8
$2,4,6\text{-}(CH_3)_3C_6H_2NO$	107.4 ± 1.9 (7)	106.5 ± 2.6	0.9 ± 3.2
$2,6\text{-}(C_2H_5)_2C_6H_3NO$	100.1 ± 3.4	$100.6 \pm [3.3]$	$-0.5 \pm [4.7]$
$2,4,6\text{-}\{CH_3C(CH_3)_2\}_3C_6H_2NO$	-117.4 ± 5.4	-110.6 ± 4.3	-6.8 ± 6.9
$4\text{-}(CH_3)_2NC_6H_4NO$	185.0 ± 2.3 (6)	222.9 ± 5.2	-37.9 ± 5.7

TABLE 5. Observed and calculated $\Delta_f H_m^\circ(g)$ values for nitrobenzene derivatives

	$\Delta_f H_m^\circ(g)/(\mathrm{kJ \cdot mol^{-1}})$ observed	$\Delta_f H_m^\circ(g)/(\mathrm{kJ \cdot mol^{-1}})$ calculated	$\frac{\Delta\Delta_f H_m^\circ}{\mathrm{kJ \cdot mol^{-1}}}$
$4\text{-}CH_3C_6H_4NO_2$	31.0 ± 3.8 (24)	35.3 ± 1.1	-4.3 ± 4.0
$2,6\text{-}(CH_3)_2C_6H_3NO_2$	8.6 ± 1.6 (7)	2.2 ± 1.2	6.4 ± 2.0
$2\text{-}(C_2H_5)C_6H_4NO_2$	11.2 ± 6.6 (24)	14.8 ± 1.4	-3.6 ± 6.7
$4\text{-}(C_2H_5)C_6H_4NO_2$	7.4 ± 6.6 (24)	14.8 ± 1.4	-7.4 ± 6.7
$2,4,6\text{-}\{CH_3C(CH_3)_2\}_3C_6H_2NO_2$	-189.9 ± 4.4	-248.1 ± 3.8	58.2 ± 5.8

that within the limits of uncertainty, 2,4,6-tri(1,1-dimethylethyl)nitrosobenzene has an expected enthalpy of formation thus showing neither strain nor stabilization energy.

A similar exercise for $C_6H_5NO_2$ derivatives is presented in table 5: to derive the calculated values the following additional $\Delta_f H^\circ_m(g)/(kJ\cdot mol^{-1})$ values were used: $C_6H_5NO_2$, (67.5 ± 0.6);(24) $C_6H_5CH_3$, (50.4 ± 0.6);(24) $C_6H_5C_2H_5$, (29.9 ± 1.1).(24) From the comparison in table 5 it is clear that 2,4,6-tri(1,1-dimethylethyl)nitrobenzene exhibits very large steric-strain energy.

If 2,4,6-tri(1,1-dimethylethyl)nitrosobenzene were to dimerize, it would seem reasonable to assume that the steric-strain energy in the dimer would be at least twice that shown by the nitroderivative, *i.e.* $\approx 116\ kJ\cdot mol^{-1}$. As $D_m(N{=}N)$ in $C_6H_5N(O)\cdot N(O)\cdot C_6H_5$ is $(91.1 \pm 8.5)\ kJ\cdot mol^{-1}$,(7) it is clear that steric hindrance prevents formation of the dimer of 2,4,6-$\{CH_3C(CH_3)_2\}_3C_6H_2NO$ in contrast to the case of 4-$N(CH_3)_2C_6H_4NO$ where exceptional stabilization of the monomer prevents dimerization.(6)

The determination of $D_m(N–O)$ in a nitrocompound is $\Delta_r H^\circ_m(g)$ for $RNO_2 = RNO + O$, requiring $\Delta_f H^\circ_m(O,g) = (249.17 \pm 0.10)\ kJ\cdot mol^{-1}$.(22) For 2,4,6-$\{CH_3C(CH_3)_2\}_3C_6H_2NO_2$, $D_m(N–O) = (321.8 \pm 7.0)\ kJ\cdot mol^{-1}$, a marked reduction from that in $C_6H_5NO_2$ of $(391.5 \pm 8.0)\ kJ\cdot mol^{-1}$.(7) This shows the very large effect of steric hindrance of the two 1,1-dimethylethyl groups *ortho* to the nitro group as the X-ray analysis has shown that the nitro group has been forced from its preferred orientation planar with the benzene ring to be perpendicular to the ring, hence eliminating any stabilization effect of π-electron delocalization between the nitro group and the benzene ring.

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