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## Key indicators

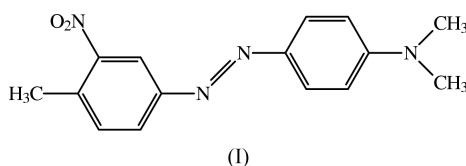
Single-crystal X-ray study  
*T* = 193 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
*R* factor = 0.055  
*wR* factor = 0.154  
Data-to-parameter ratio = 12.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Redetermination of *N,N*-dimethyl-*N*-[4-[(*E*)-(4-methyl-3-nitrophenyl)diazenyl]phenyl]amine at 193 K: another example of dynamic disorder of substituted azo-benzene compoundsRedetermination of the title compound,  $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_2$ , at 193 K reveals considerable differences in geometry of the central bridging fragment as compared to that at 293 K [Atroshchenko, Blokhina, Shakel'dyan, Grudtsyn, Gitis, Borbulevich, Blokhin, Kaminskii, Shishkin & Andrianov (2000). *Russ. J. Org. Chem.* **36**, 684–692]. The results show that there is apparent shortening of the  $\text{N}=\text{N}$  bond and lengthening of both neighbouring  $\text{C}-\text{N}$  bonds in the room-temperature structure compared with the low-temperature structure.

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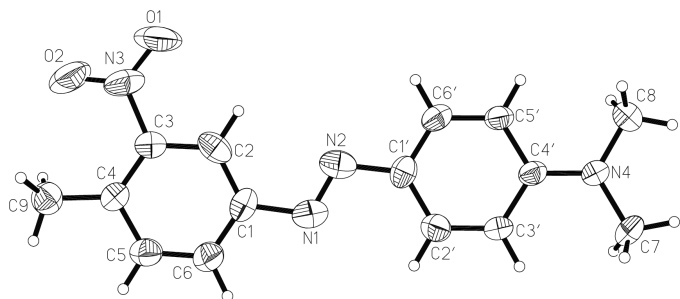
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## Comment

As part of developing a new route for the synthesis of nitro-azobenzenes based on reactions between arenediazonium and corresponding anionic  $\sigma$ -complexes, an X-ray study of the title compound, (I), was carried out at 293 K; in this an unusual geometry of the central bridging  $\text{C1}-\text{N1}-\text{N2}-\text{C1}'$  fragment of the molecule was observed (Atroshchenko *et al.*, 2000). In particular, the  $\text{N1}=\text{N2}$  bond in (I) at 293 K [1.188 (3)  $\text{\AA}$ ] was considerably shorter than the typical  $\text{N}=\text{N}$  bond length (1.25  $\text{\AA}$ ; Allen *et al.*, 1987) for *trans*-azoarenes. Moreover, the  $\text{C1}-\text{N1}$  and  $\text{C1}'-\text{N2}$  bonds in (I) at 293 K were elongated to 1.516 (4) and 1.492 (4)  $\text{\AA}$ , respectively, compared with the average bond length (1.43  $\text{\AA}$ ; Allen *et al.*, 1987).

However, a literature review reveals several examples of a similar shortening of both the  $\text{N}=\text{N}$  and  $\text{C}=\text{C}$  bonds of bridging fragments, *e.g.* in (*E*)-azobenzene (Harada *et al.*, 1997), (*E*)-stilbene (Bernstein, 1975; Hoekstra *et al.*, 1975), (*E*)-2,20-dimethylstilbene (Ogawa *et al.*, 1988, 1992) and indole-substituted pyridinium iodide salts (Wang *et al.*, 2001). For instance, the X-ray investigation of (*E*)-azobenzene (Harada *et al.*, 1997) showed that the  $\text{N}=\text{N}$  bond of the one independent molecule in this structure at room temperature is significantly shorter than at 82 K [1.189 (6) and 1.251 (2)  $\text{\AA}$ , respectively]. Recent multi-temperature investigations of this phenomenon (Harada *et al.*, 1995, 1997) led to the conclusion that shrinkage of these double bonds is an artifact of torsional vibration of the  $\text{C}(\text{or N})-\text{Ph}$  bond. If the amplitude of the torsional vibration is large enough, it gives rise to conformational interconversion and hence dynamic disorder in the crystal. However, such dynamic disorder cannot usually be resolved in a routine experiments because of the low resolu-



**Figure 1**

A view of compound (I). The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level.

tion of the X-ray data and the low population of one of the conformers (Harada *et al.*, 1997; Wang *et al.*, 2001).

Thus, similar dynamic disorder could take place in structure (I) at room temperature, resulting in the abnormal values of the C–N and N=N bonds mentioned above. To verify this suggestion, an X-ray study of (I) was carried out at 193 K. This low-temperature investigation indicates (Table 1) that the N1=N2 bond length is considerably elongated while the lengths of both the C–N bonds in question are decreased in comparison to their values in (I) at 293 K. These bond lengths in (I) at 193 K are therefore close to typical values (Allen *et al.*, 1987) and these low-temperature data unambiguously confirm the dynamic nature of the disorder in (I). It should also be mentioned that the C3–N3 bond length [1.470 (3) Å] of the nitro group in (I) at 193 K, being close to the standard value for this type of bond (Allen *et al.*, 1987), is noticeably longer than that in the room-temperature structure [1.438 (4) Å; Atroshchenko *et al.*, 2000]. This shortening of the C3–N3 bond at 293 K may probably be attributed to the intensive librational motion of atoms in the corresponding fragment of the molecule. No other essential differences between the low- and high-temperature structures of (I) are observed.

## Experimental

The synthesis procedure of (I) and the corresponding IR and  $^1\text{H}$  NMR spectrum data have already been reported (Atroshchenko *et al.*, 2000).

### Crystal data

$\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_2$   
 $M_r = 284.32$   
 Monoclinic,  $P2_1/c$   
 $a = 10.509$  (6) Å  
 $b = 10.763$  (5) Å  
 $c = 13.146$  (7) Å  
 $\beta = 107.26$  (4)°  
 $V = 1420.0$  (13) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.330$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 24 reflections  
 $\theta = 10\text{--}11^\circ$   
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 193$  (2) K  
 Prism, red  
 $0.40 \times 0.20 \times 0.20$  mm

### Data collection

Syntex  $P2_1/PC$  diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction: none  
 2591 measured reflections  
 2447 independent reflections  
 1229 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.049$

$\theta_{\text{max}} = 25.1^\circ$   
 $h = 0 \rightarrow 12$   
 $k = 0 \rightarrow 12$   
 $l = -15 \rightarrow 14$   
 2 standard reflections  
 every 98 reflections  
 intensity decay: 3.7%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.055$   
 $wR(F^2) = 0.154$   
 $S = 0.87$   
 2447 reflections  
 193 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0998P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.19$  e Å<sup>-3</sup>

**Table 1**

Selected interatomic distances (Å).

N1–N2	1.239 (3)	N2–C1'	1.437 (3)
N1–C1	1.462 (3)		

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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