PERKIN 2

Low-temperature X-ray structural analysis of propanedinitrile derivatives substituted with a bis(4-dimethylaminophenyl)methyl group: the origin of elongation of the donor–acceptor substituted C–C bond †

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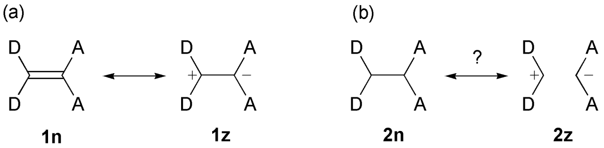
Push–pull type substitution at C$_{sp^3}$–C$_{sp^3}$ in the title compounds does not have special electronic effects on the bond length, and the observed expansion can be best accounted for by steric interaction between substituents.

Introduction

Recently, much attention has been focused on molecules that have both electron-donating (D) and -accepting (A) moieties[1] (*e.g.* **1**) for use as NLO materials[2] or for NIR-absorption[3] and electrical rectification.[4] All of these properties are related to their polarizability due to π-conjugation between the D and A units (Scheme 1a). It is the general view that the bond order in **1** is decreased by the contribution of a zwitterionic form **1z**.

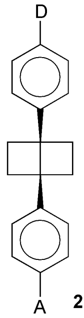


D = electron-donating group; A = electron-accepting group

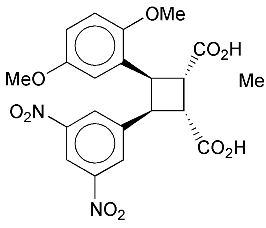
Scheme 1

In contrast, the situation is not so simple in **2**, where D and A are connected by a C$_{sp^3}$–C$_{sp^3}$ single bond. Based on MNDO calculations,[5] the donor–acceptor substituted C^1–C^4 bond in bicyclo[2.2.0]hexanes **2a′** was first predicted to be elongated or even broken to give an ion pair as in **2z**. However, this idea has recently been questioned using the *ab initio* technique.[6] In the crystallographic studies on some push–pull compounds with a cyclobutane [**2b′**: 1.566(5) Å[7a]] or a bicyclo[3.3.0] skeleton [**2c′**: 1.618(3) Å[7b]],‡ C$_{sp^3}$–C$_{sp^3}$ distances greater than the standard (1.54 Å)[8] were rationalized by the former theoretical prediction § based on through-bond (TB) interaction,[11] but the expansion of the donor–acceptor substituted C^9–C^{10} bond observed in dihydrophenanthrene **3** was accounted for by steric repulsion rather than by electronic/orbital interaction between the substituents.[12] It is still unclear whether or not the differences in steric and electronic effects may arise from the ring size to which the push–pull substituted C$_{sp^3}$–C$_{sp^3}$ bond is involved (4, 5, or 6 membered ring in **2b′**, **2c′**, and **3**).

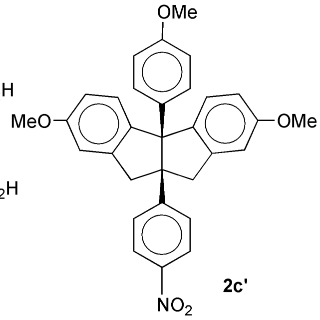
To get more insight into this controversial problem and address the question of whether push–pull type substitution plays a role in C–C elongation by enhanced (π–σ*)-type TB interaction, we planned the low-temperature X-ray analysis of a new series of compounds, in which the same push–pull substituents to **3** are framed into different structures [D = 4-dimethylaminophenyl (≡Ar); A = CN]. These groups were again selected here in anticipation of enough stabilization effects to detect the ion pair **2z** [pK_R^+ of Ar$_2$CPh$^+$ = 6.90; pK_a of CH$_2$(CN)$_2$ = 11.0]. The title compounds **4**–**6** were designed in this way and newly prepared for this purpose, and their precise molecular structures are reported herein along with those of the π-conjugated system **7**[13] for comparison.



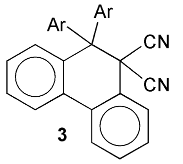
2a'



2b'



2c'



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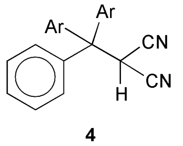

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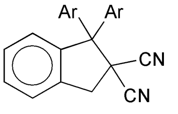

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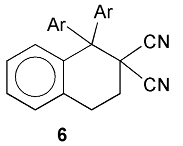

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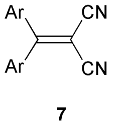

7

Ar = 4-Me$_2$NC$_6$H$_4$

Results and discussion

Preparation and photoreactivity of push–pull compounds

Reaction of Malachite Green BF$_4^-$ salt with an excess amount of malononitrile in the presence of Et$_3$N gave colorless crystals

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† Electronic supplementary information (ESI) available: atom numbering schemes for **4**–**7**. See http://www.rsc.org/suppdata/p2/b1/b103269k/

‡ It was pointed out that the substituent effects on the central bond length in 1,5-diarylbicyclo[3.3.0]octanes are calculated to be very small at the AM1 level, thus suggesting the necessity for experimental evaluation of the push–pull effect.[7b]

§ While several recent reports suggest that there is no relation between C$_{sp^3}$–C$_{sp^3}$ bond elongation and TB interaction,[6,9] this issue is still a subject of controversy.[10]

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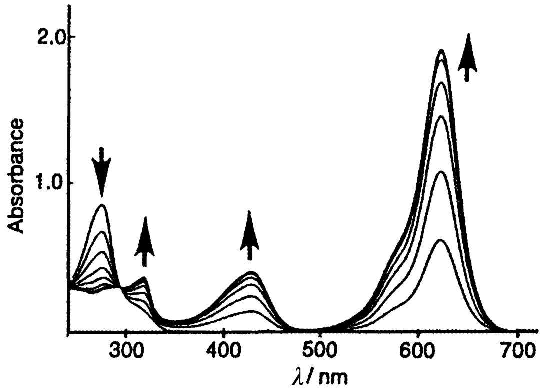


Fig. 1 Changes in the UV–VIS spectrum of **4** (2.40×10^{-5} mol dm^{-3} in CH_2Cl_2) upon photoirradiation ($\lambda = 254 \pm 10$ nm) by a 150 W Xe lamp at 10 min intervals. Similar changes occurred within a minute when the same solution was irradiated by a 100 W low-pressure Hg lamp.

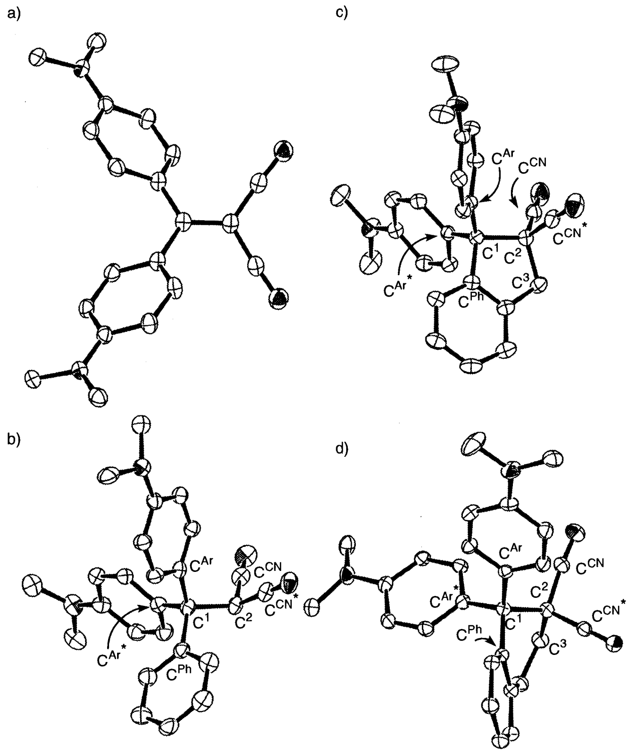
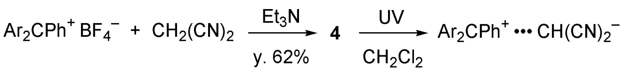


Fig. 2 ORTEP drawing of push–pull compounds. Note the absence of any structural disorder in these structures: a) **7**; b) **4** (molecule-1); c) **5**; d) **6**.

of ‘acyclic’ derivative **4**, in which the CAr_2–$C(CN)_2$ bond is not confined in a ring structure (Scheme 2). The ^{13}C NMR chemical

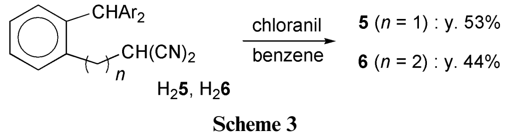


$$Ar_2CPh^+ BF_4^- + CH_2(CN)_2 \xrightarrow[\text{y. 62\%}]{Et_3N} \mathbf{4} \xrightarrow[CH_2Cl_2]{UV} Ar_2CPh^+ \cdots CH(CN)_2^-$$

Scheme 2

shifts [δ 58.44 ppm for *C*Ar_2; 35.86 ppm for *C*$(CN)_2$ in $CDCl_3$] indicate the negligible contribution of a polarized form such as **2z** in the ground state. However, upon UV-irradiation of **4** in CH_2Cl_2, a deep blue color characteristic of Ar_2CPh^+ (λ_{max} 621 nm) developed rapidly with an isosbestic point (Fig. 1). Such a photochromic behavior indicates that the CAr_2–$C(CN)_2$ bond undergoes heterolysis *via* the excited state.

Indane and tetralin derivatives **5** and **6** were obtained as colorless crystals from the corresponding open-chain dihydro compounds (H_2**5** and H_2**6**) by oxidative CAr_2–$C(CN)_2$ bond formation (Scheme 3). In contrast to **4**, these cyclic compounds



Scheme 3

did not show strong coloration upon irradiation, probably due to rapid cyclization of the bond-dissociated photoproducts to form a 5- or 6-membered ring. Further photoirradiation caused consumption of **5** and **6** without giving definable products.

In any event, successful preparation of **4**–**6** by the CAr_2–$C(CN)_2$ bond-forming procedures clearly shows this bond is robust enough under the reaction conditions.

Low-temperature X-ray analyses

A crystallographic study was first conducted on a violet crystal of olefin **7** at −150 °C to confirm that the selected D and A units are strong enough to induce polarization of the C_{sp^2}=C_{sp^2} bond (Scheme 1a). The observed bond length [1.392(4) Å] is close to those found in benzene derivatives (1.38 Å)[8] and much longer than that of a pure double bond (1.33 Å),[8] indicating a significant contribution of a polarized structure. Twisting around the central bond [21.1(1)°] is consistent with the reduced π-bond order (Fig. 2a). With these results in mind, X-ray analyses were also carried out on **4**–**6** with a donor–acceptor substituted C_{sp^3}–C_{sp^3} bond at −150 °C (Table 1, Fig. 2b–2d).

The CAr_2–$C(CN)_2$ distance (d_1) in tetralin **6** is 1.600(2) Å, which is identical to that of dihydrophenanthrene **3** [1.599(4) Å at −70 °C].[12] In the case of acyclic **4**, almost the same values of d_1 [1.596(5) and 1.595(5) Å] are observed for the two crystallographically independent molecules. Such a similarity among **3**, **4** (molecule-1), **4** (molecule-2), and **6** clearly shows that the intrinsic value of d_1 is *ca.* 1.60 Å, which is scarcely affected by a crystal packing force or other structural features such as whether or not this bond is involved in a ring system.

Elongation of CAr_2–$C(CN)_2$ beyond the standard C_{sp^3}–C_{sp^3} (1.54 Å)[8] can be rationalized either by repulsive steric interaction between the substituents or by special electronic effects through (π–σ*)-type TB interaction. When the latter interaction is more important, the flanking bonds (d_2, d_3, $d_{3'}$, d_4, $d_{4'}$) are expected to be shortened.[14] However, all of them are greater than or nearly equal to the standards (C_{sp^3}–C_{Ar}, 1.51 Å; C_{sp^3}–C_{CN}, 1.47 Å)[8] indicating that bond expansion would be the result of steric interaction.¶

The further bond elongation of CAr_2–$C(CN)_2$ observed in indane **5** [d_1: 1.630(3) Å] strongly supports this explanation.‖ The largest geometrical difference between **5** and others is found in the torsion angle (φ_1) through this bond, which is much smaller in **5** [19.2(2)°] than in the 6-membered ring compounds [**6**: 70.1(1)°; **3** : 63.2(3)°[12]].

Restricted torsion around CAr_2–$C(CN)_2$ in **5** causes much greater ‘front’ strain[15] between the substituents than in others, which may account for the additional expansion of this bond by 0.03 Å. Comparisons of non-bonded distances between push–pull substituents (d_5, $d_{5'}$, $d_{5''}$) indicate that the closest C···C contant [2.68(1) Å] is found in indane **5**.

Another difference is the degree of antiperiplanarity of the Ar* and CN* groups as estimated by φ_2 in Table 1. The smallest value in **5** indicates that this molecule is least suitable for TB interaction from the viewpoint of the ‘*trans* rule’[16] although **5** has the longest CAr_2–$C(CN)_2$ bond among **3**–**6**. This result also

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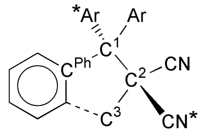
¶ Although the cylinder-shaped cyano group is seldomly regarded as a space-requiring substituent, the extended Y-shaped dicyanomethyl or dicyanomethylene group sometimes induces significant deformation of molecular structures. Elongation of the C^9–C^{10} bond in 9,9,10,10-tetracyano-9,10-dihydrophenanthrene [1.587(2) Å] was also accounted for by steric interaction.[12]

‖ *Ab initio* calculation on **5** at B3LYP/6-31G* level indicates a similar degree of bond elongation for the CAr_2–$C(CN)_2$ unit (1.628 Å).

Table 1 Geometric parameters for **4**–**6** determined by X-ray analyses at 123 K[a]



	4 (molecule-1)[b]	**4** (molecule-2)[b]	**5**	**6**
d_1 (C^1–C^2)/Å	1.596(5)	1.595(5)	1.630(3)	1.600(2)
d_2 (C^1–C^{Ph})/Å	1.550(5)	1.545(5)	1.521(3)	1.537(2)
$d_{2'}$ (C^2–C^3)/Å	—	—	1.557(3)	1.549(2)
d_3 (C^1–C^{Ar*})/Å	1.539(5)	1.536(5)	1.544(3)	1.536(2)
$d_{3'}$ (C^1–C^{Ar})/Å	1.528(5)	1.535(5)	1.525(3)	1.540(2)
d_4 (C^2–C^{CN*})/Å	1.488(5)	1.468(5)	1.484(3)	1.486(2)
$d_{4'}$ (C^2–C^{CN})/Å	1.478(5)	1.474(5)	1.474(3)	1.482(2)
d_5 ($C^{Ar} \cdots C^{CN*}$)/Å[c]	2.86(1)	2.89(1)	2.68(1)	3.18(1)
$d_{5'}$ ($C^{Ar*} \cdots C^{CN}$)/Å[c]	2.77(1)	2.79(1)	2.83(1)	3.23(1)
$d_{5''}$ ($C^{Ar} \cdots C^{CN}$)/Å[c]	3.31(1)	3.28(1)	3.38(1)	2.94(1)
φ_1 (C^{Ph}–C^1–C^2–C^3)/°	—	—	19.2(2)	70.1(1)
φ_2 (C^{Ar*}–C^1–C^2–C^{CN*})/°	159.7(3)	162.6(3)	149.2(2)	164.4(1)

[a] One of two aryl groups (Ar*) and one of two cyano groups (CN*) are arranged in a nearly antiperiplanar manner (φ_2 = *ca.* 180°) (Ar = Ar* = 4-$Me_2NC_6H_4$). [b] Two crystallographically independent molecules are denoted as molecule-1 and -2. In contrast to cyclic compounds, deformation for angles C^1–C^2–C^{CN*} [112.5(3), 113.8(3)°] and C^1–C^2–C^{CN} [113.2(3), 113.5(3)°] was observed that seems to be the results of 'front' strain. [c] Values of d_5, $d_{5'}$, and $d_{5''}$ for dihydrophenanthrene **3** (203 K) are 2.92(1), 2.81(1), and 3.09(1) Å, respectively.

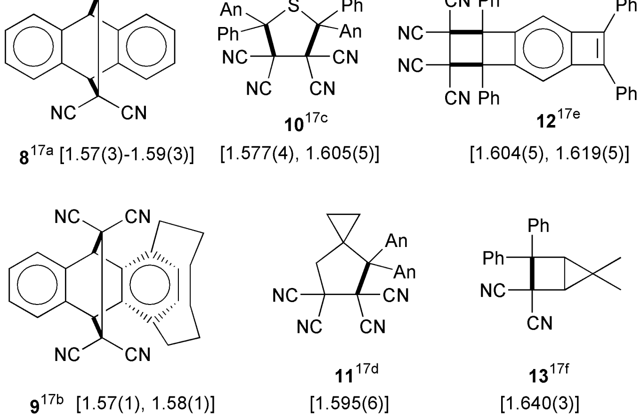
conflicts with the assumption that the bond elongation is caused by TB interaction.

We found no evidence to suggest that push–pull type substitution on C_{sp^3}–C_{sp^3} in **4**–**6** has any special bond-elongation effects, even if the same substitution induces significant polarization of the C_{sp^2}=C_{sp^2} bond in **7**. We conclude that the observed expansion of CAr_2–$C(CN)_2$ (1.60–1.63 Å) to beyond the standard is the result of steric hindrance between bulky aryl and dicyanomethyl substituents.

Database study

In order to further support our conclusion, the Cambridge Structural Database (version 5.21) was surveyed to find structural data of reference compounds that have the $C_{sp^3}(aryl)_2$–$C_{sp^3}(CN)_2$ unit. None of the retrieved six structures (**8**–**13**)[17] has a very strong donating group like Me_2N.

All of the C–C bonds in question are longer than the standard (Scheme 4). Further inspection indicates that the bond expansion in the anthracene–TCNE adducts (**8** and **9**) is not prominent (1.57–1.59 Å) although their bicyclo[2.2.2] skeleton is favorable for TB interaction due to the suitable orientation of orbitals. In contrast, the bond lengths in the four-membered-ring compounds **12** and **13** are beyond 1.6 Å. The very long bond in the housane derivative **13** [1.640(3) Å] can be accounted for by the large steric strain between substituents, which is in line with our conclusion.



Scheme 4

Experimental

Preparation of push–pull compounds

To a solution of malononitrile (238 mg, 3.61 mmol) in dry MeCN (30 mL) was added Et_3N (0.50 mL, 3.59 mmol). After stirring for 15 min, bis(4-dimethylaminophenyl)(phenyl)carbenium tetrafluoroborate (0.5 equiv. THF solvate, 150 mg, 0.33 mmol) was added at once, and the whole mixture was stirred for 3 min. After dilution with water and extraction with benzene, the organic layer was washed with brine and dried over Na_2SO_4. Evaporation of solvent followed by chromatographic separation on SiO_2 (ether–benzene = 1 : 10) gave 2-[α,α-bis(4-dimethylaminophenyl)benzyl]propanedinitrile **4**. This material was further purified by recrystallization from MeOH to give colorless crystals of **4** (80 mg) in 62% yield.

To a solution of 2-{2-[bis(4-dimethylaminophenyl)methyl]benzyl}propanedinitrile H_2**5** (19 mg, 0.047 mmol) in dry benzene (1 mL) was added chloranil (12 mg, 0.049 mmol), and the mixture was heated at reflux for 2.5 h. Insoluble material was removed by filtration and washed with hot benzene. The filtrate was concentrated and separated by preparative thick layer chromatography (SiO_2; 0.05 × 20 × 20 cm; AcOEt–$CHCl_3$ = 5 : 95; R_f = 0.47–0.56) to give colorless crystals of 1,1-bis(4-dimethylaminophenyl)indane-2,2-dinitrile **5** (10 mg) in 53% yield. Similarly, 2-{2-[bis(4-dimethylaminophenyl)methyl]phenethyl}propanedinitrile H_2**6** was convereted to colorless crystals of 1,1-bis(4-dimethylaminophenyl)-1,2,3,4-tetrahydronaphthalene-2,2-dinitrile **6** in 44% yield.

Data for **4**: mp 163.0–164.5 °C (Found: C, 79.0; H, 6.7; N, 14.0. Calcd for $C_{26}H_{26}N_4$: C, 79.2; H, 6.6; N, 14.2%); λ_{max} (CH_2Cl_2)/nm 276 (log ε 4.52); δ_H (400 MHz; $CDCl_3$, 24 °C; TMS) 7.26–7.36 (5H, m), 7.09 (4H, AA′XX′), 6.66 (4H, AA′XX′), 5.03 (1H, s), 2.95 (12H, s); δ_C (75 MHz; $CDCl_3$) 149.55, 143.07, 129.58, 129.38, 128.60, 128.42, 127.57, 113.10, 111.77, 58.44, 40.20, 35.86; ν_{max} (KBr)/cm^{-1} 2892, 2248, 1612, 1358, 814; *m*/*z* (FD) 394 (M^+).

Data for **5**: mp 245.0–247.0 °C (Found: C, 78.4; H, 6.55; N, 13.25. Calcd for $C_{27}H_{26}N_4 \cdot 0.5H_2O$: C, 78.0; H, 6.55; N, 13.5%); λ_{max} (CH_2Cl_2)/nm 274 (log ε 4.62); δ_H (300 MHz; $CDCl_3$; TMS)

7.34–7.30 (4H, m), 7.26 (4H, AA′XX′), 6.64 (4H, AA′XX′), 3.90 (2H, s), 2.94 (12H, s); ν_{max} (KBr)/cm^{-1} 2880, 2804, 2244, 1612, 1522, 1360, 800, 746, 568; *m*/*z* (FD) 406 (M^+).

Data for **6**: mp 211.0–212.5 °C (Found: C, 78.4; H, 6.7; N, 12.8; Calcd for $C_{27}H_{26}N_4\cdot 0.5H_2O$: C, 78.3; H, 6.8; N, 13.05%); λ_{max} (CH_2Cl_2)/nm 274 (log ε 4.57); δ_H (300 MHz; $CDCl_3$; TMS) 7.27–7.24 (1H, m), 7.22–7.17 (5H, m), 7.10 (1H, ddd, $J = 7.5$, 7.5, 1.0 Hz), 6.85 (1H, dd, $J = 7.5$, 1.0 Hz), 6.65 (4H, AA′XX′), 3.09 (2H, t, $J = 7.4$ Hz), 2.96 (12H, s), 2.44 (2H, t, $J = 7.4$ Hz); ν_{max} (KBr)/cm^{-1} 2892, 1484, 1448, 1216, 1168, 814, 764; *m*/*z* (FD) 422 (M^+).

Crystallographic study **

Data collection was conducted by a Rigaku Mercury CCD apparatus with Mo-Kα radiation at 123 K (a liquid N_2 flow method). Crystallographic data are as follows.

4: $C_{26}H_{26}N_4$, *M* 394.52, orthorhombic, $Pca2_1$, $a = 21.812(1)$, $b = 9.8235(4)$, $c = 19.7739(8)$ Å, $U = 4237.0(3)$ Å^3, D_c ($Z = 8$) = 1.237 g cm^{-1}, $\mu = 0.74$ cm^{-1}. The final *R* value is 0.051 for 3800 independent reflections with $I > 3\sigma I$ and 541 parameters. Two crystallographically independent molecules are related by a pseudo inversion center. However, refinement did not converge in the centrosymmetric space groups such as *Pbcm* or *Pbca*.

5: $C_{27}H_{26}N_4$, *M* 406.53, monoclinic, $P2_1/c$, $a = 10.504(3)$, $b = 15.414(1)$, $c = 13.7027(6)$ Å, $\beta = 102.315(1)°$, $U = 2167.4(7)$ Å^3, D_c ($Z = 4$) = 1.246 g cm^{-1}, $\mu = 0.75$ cm^{-1}. The final *R* value is 0.051 for 3125 independent reflections with $I > 3\sigma I$ and 280 parameters.

6: $C_{28}H_{28}N_4$, *M* 420.56, monoclinic, $P2_1/n$, $a = 9.490(1)$, $b = 23.201(2)$, $c = 10.4463(3)$ Å, $\beta = 99.1048(6)°$, $U = 2271.0(3)$ Å^3, D_c ($Z = 4$) = 1.230 g cm^{-1}, $\mu = 0.74$ cm^{-1}. The final *R* value is 0.054 for 4169 independent reflections with $I > 3\sigma I$ and 289 parameters.

7: $C_{20}H_{20}N_4$, *M* 316.40, monoclinic, *C*2/*c*, $a = 11.804(3)$, $b = 9.299(2)$, $c = 15.358(1)$ Å, $\beta = 98.440(2)°$, $U = 1667.5(5)$ Å^3, D_c ($Z = 4$) = 1.260 g cm^{-1}, $\mu = 0.77$ cm^{-1}. The final *R* value is 0.048 for 1342 independent reflections with $I > 3\sigma I$ and 110 parameters. Molecule is located on a crystallographic 2-fold axis.

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