

## Electronic Structure and Conformational Properties of Azines. Part 2.<sup>1</sup> 2,5-Diacetyl-3,4-diazahexa-2,4-diene, a 2,3-Diaza-1,3-diene with a Synclinal Conformation: an X-Ray Crystallographic, He<sup>I</sup> Photoelectron Spectroscopic, and MNDO Study

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2,5-Diacetyl-3,4-diazahexa-2,4-diene consists of two essentially planar halves that are twisted about each other by 102.7°. Bond lengths and orbital energies indicate strong conjugation between the electron lone-pair of one nitrogen atom and the double bonds of the other half of the molecule. The molecular structure and torsion around the N–N and C–C bonds have been studied by MNDO calculations. While the structure parameters are in reasonable agreement with experimental values, conformational properties are not treated adequately. According to these calculations orbital energies are nearly invariant to conformational changes.

The conformational properties of 1,3-dienes and hetero-1,3-dienes have been studied extensively by experimental and theoretical methods. For buta-1,3-diene<sup>2,3</sup> in addition to the planar *anti* form a small amount of a second conformer has been detected by spectroscopic methods. The symmetry of the less stable conformer is still subject to controversial discussion. Recent *ab initio* results are in favour of a  $C_2$  form with a torsional angle of *ca.* 35° relative to the planar *syn* form.<sup>2</sup>

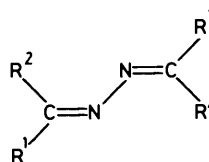
Acrolein<sup>4</sup> and glyoxal,<sup>5,6</sup> where, compared with buta-1,3-diene, one or two methylene groups, respectively, have been replaced by oxygen atoms, show the same qualitative conformational behaviour as the parent molecule: In both cases the *anti* form is by far the prevailing conformer. The less stable *syn* forms, however, are also planar.

Substitution of the methine groups of a 1,3-diene by nitrogen atoms leads to an azine, the parent compound being 2,3-diazabuta-1,3-diene (1). The unique chemical properties<sup>7</sup> as well as the conformational behaviour of these compounds<sup>1</sup> are determined, at least to a large extent, by the vicinal electron lone-pairs in addition to the conjugated double bonds.

An electron diffraction analysis of the molecular structure of (1)<sup>8</sup> led to an *anti-gauche* equilibrium, in which the former conformer dominates (*ca.* 80% at 60 °C). According to a study by the same method for 3,4-diazahexa-2,4-diene (2)<sup>9</sup> a small amount of a *gauche* (or synclinal) form is present besides the *anti* conformer, whereas the tetrabromo derivative (5)<sup>10</sup> is exclusively in the *gauche* conformation. For azine (7)<sup>11</sup> a planar centrosymmetric structure was found by X-ray analysis.

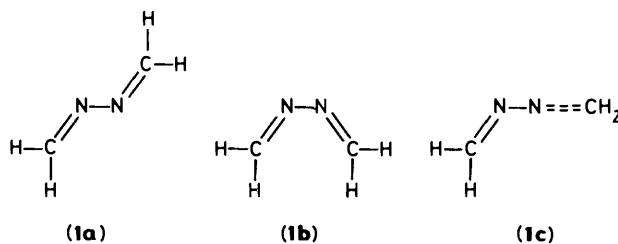
Vibrational spectroscopy indicated planar *anti* conformations for azines (4),<sup>12</sup> (2),<sup>13</sup> and (3).<sup>14</sup> These results were confirmed by photoelectron (p.e.) spectroscopy for (1)–(3), and other azines of acyclic and cyclic aliphatic ketones.<sup>1</sup> The p.e. spectra of aromatic azines<sup>15</sup> are also consistent with planar *anti* conformations.

The torsional potential of (1) has been calculated by various quantum mechanical methods.<sup>1,16,17</sup> Besides the global minimum of the *anti* form in one case only<sup>16</sup> a minimum for a *gauche* conformation has been obtained. Therefore, and with respect to the spectroscopic findings,<sup>1</sup> the existence of a second conformer of (1) in addition to the *anti* form remains uncertain.



- (1)  $R^1 = R^2 = H$
- (2)  $R^1 = CH_3, R^2 = H$
- (3)  $R^1 = R^2 = CH_3$
- (4)  $R^1 = R^2 = F$
- (5)  $R^1 = R^2 = Br$
- (6)  $R^1 = COCH_3, R^2 = CH_3$
- (7)  $R^1 = C_6H_5, R^2 = H$

*Electronic Structure and Conformational Properties of Substituted Azines.*—By perturbation theory<sup>18</sup> a simple model can be constructed for the relation between electronic structure and conformational properties of azines. Qualitatively the MOs of (1) can be obtained by the combination of two methane imine units.<sup>1</sup> The most important contributions to the relative stabilities of *syn*, *anti*, and *gauche* forms of (1) are interactions between the  $n$ ,  $\pi$ , and  $\pi^*$  orbitals of the two imine fragments.



The planar conformations (1a and b) are stabilized by  $\pi/\pi^*$  interaction. The *syn* conformation (1b) obviously is destabilized due to strong interactions of the vicinal electron lone pairs, electrostatic effects, and steric repulsion of the two *endo*

Table 1. MNDO results for different conformations of azine (6)

$\theta_1$ (°)	$\theta_2 = \theta_3$ (°)	$\Delta H_f/\text{kJ mol}^{-1}$	$-\epsilon$ (eV)								
			$n_N$ (a)	$\pi_{C=N}$ (b)	$n_O$ (b)	$n_O$ (a)	$\pi_{C=O}$ (a)	$\pi_{C=O}$ (b)	$n_N$ (b)	$\pi_{CH_3}$ (a)	$\pi_{C=N}$ (a)
180	180	-163.8	10.41	10.60	11.21	11.34	13.32	13.44	13.55	13.66	13.76
150	180	-164.2	10.41	10.70	11.21	11.33	13.32	13.44	13.61	13.69	13.75
120	180	-163.3	10.42	10.91	11.22	11.29	13.32	13.43	13.73	13.68	13.78
110	180	-162.0	10.43	10.99	11.23	11.27	13.32	13.43	13.77	13.66	13.80
100	180	-159.9	10.43	11.05	11.23	11.25	13.31	13.42	13.80	13.63	13.81
90	180	-156.9	10.44	11.09	11.24	11.22	13.30	13.41	13.82	13.61	13.82
180	150	-185.9	10.42	10.59	11.20	11.34	13.37	13.43	13.67	13.71	13.76
180	120	-204.6	10.36	10.56	11.18	11.31	13.39	13.40	13.56	13.84	13.71
180	90	-207.8	10.26	10.52	11.13	11.27	13.40	13.33	13.70	13.92	13.71
149.8	92.4	-213.2	10.29	10.59	11.14	11.28	13.40	13.36	13.80	13.95	13.58

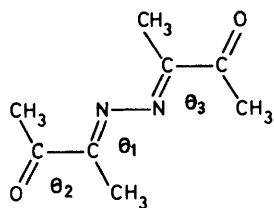


Figure 1. Definition of torsion angles in azine (6)

hydrogen atoms. This probably is the reason why unprotonated azines undergo criss-cross cycloaddition instead of [4 + 2] cycloaddition.<sup>7</sup>  $n/\pi^*$  Interaction can stabilize the *gauche* conformation (1c). This type of interaction will compete with  $\pi/\pi^*$  interaction only if the energy of the  $\pi^*$  orbital is close enough to the energy of the  $n$  orbital.

Alkyl substituents on the  $sp^2$  carbon atom of an imine destabilize the  $\pi$  MO more than the  $n$  MO. This is clearly indicated by the first two ionization potentials ( $n_N$  and  $\pi$ ) of simple aliphatic imines.<sup>19</sup> Consequently, in an azine the *gauche* conformation is destabilized by alkyl substitution in favour of the *anti* form, which is the only conformer detected by spectroscopic methods.<sup>1,12-14</sup> Also in azines the  $\pi$  MOs are more destabilized by alkyl substitution than the  $n$  MOs.<sup>1</sup>

As is known from p.e.<sup>20</sup> and electron transmission spectroscopy,<sup>21</sup> acetyl groups stabilize  $\pi$  and  $\pi^*$  MOs by ca. 0.5 and 1.5 eV,<sup>20</sup> respectively. Effects of this size are also to be expected for the corresponding MOs of acetyl-substituted imines. On the other hand, the  $n$  orbital will interact with  $\sigma$  orbitals of the acetyl group, which will raise its energy by ca. 2 eV. Due to the opposite shifts of the  $n$  and the  $\pi^*$  MO their mutual interaction is increased and the *gauche* form of the corresponding azine will be markedly stabilized and probably become the prevailing if not the only conformer.

As an example of an acetyl-substituted azine we have studied the conformational properties of 2,5-diacetyl-3,4-diazahexa-2,4-diene (6). Barany *et al.*<sup>22</sup> found an u.v. absorption band for (6) at  $\lambda_{\text{max}}$ , 244 nm ( $\epsilon$  19 500), that has to be assigned to a  $\pi-\pi^*$  transition. For a planar conjugated octatetraene a band at ca. 280 nm should be expected. This is an indication that (6) cannot be planar but should prefer a *gauche* conformation.

The effects of other substituents like halogens, amino, alkoxy, and thioalkyl groups on the conformational behaviour of azines have also been studied. We will report on these results in due course.<sup>23</sup>

**MNDO Calculations on Azine (6).**—Internal rotation in (6) around the angles  $\theta_1-\theta_3$  is of special interest. A complete study

of the torsional energy surface would be very laborious. We have performed MNDO calculations by successively varying the torsional angles under the restriction of  $C_2$  symmetry. The results are summarized in Tables 1 and 4. The torsional angle  $\theta_1$

(= C-N-N-C) (see Figure 1) was changed stepwise from 180 to 90°. The two N=C(CH<sub>3</sub>)COCH<sub>3</sub> units were kept planar (except the hydrogen atoms), *i.e.*  $\theta_2 = \theta_3 = 180^\circ$ , while all other structural parameters were optimized. In a similar way  $\theta_2$  and  $\theta_3$

(= N-C-C-O) were varied between 180 and 90°, while  $\theta_1$  was fixed at 180°. In an additional calculation all structure parameters were refined without any restriction in symmetry. The obtained geometrical data of the most stable conformation are given in Table 4. They are discussed together with the results of the X-ray analysis.

The heat of formation,  $\Delta H_f$ , of (6) is only a little changed by internal rotation around the N-N bond. The energy minimum is at  $\theta_1$  150°, close to the planar conformation. The conformation at  $\theta_1$  90° is found to be less stable by 6.9 kJ mol<sup>-1</sup>.

The energies of the relevant molecular orbitals are included in Table 1. Only very small changes are observed for the positions of most MOs. Only  $\pi_{C=N}$  (b) and  $n_N$  (b) show a sizable shift of 0.5 and 0.3 eV, respectively. Both orbitals are stabilized by torsion. These remarkable findings are of special relevance for conformational analysis by p.e. spectroscopy.<sup>24</sup> Obviously, the variations of the interactions between  $n_N$  and  $\pi_{C=N}$  orbitals with the torsional angle  $\theta_1$  are of similar magnitude, so that both the total bond energy and the energies of the most important orbitals are only little affected.

On the other hand, torsion around the angles  $\theta_2$  and  $\theta_3$  (Figure 1) has a considerable effect on the heat of formation (Table 1). Rotation of the two acetyl groups out of the molecular plane leads to a decrease of the molecular energy by 44 kJ mol<sup>-1</sup>. If the two acetyl groups are rotated in a conrotatory way ( $\theta_2 = -\theta_3$ ), nearly identical energy values are obtained for centrosymmetric conformations as for the corresponding  $C_2$  forms in disrotation ( $\theta_2 = \theta_3$ ). According to these results conjugation between the C=N and the C=O bonds has a destabilizing effect on (6). Also this type of internal rotation causes no significant shifts in orbital energies (Table 1).

The global minimum of the energy hypersurface is found at  $\theta_1$  149.8° and  $\theta_2 = \theta_3 = 92.4^\circ$ . This conformation is found to be more stable than that one at  $\theta_1$  180° and  $\theta_2 = \theta_3 = 90^\circ$  by 5.4 kJ mol<sup>-1</sup>. As shown later these findings do not coincide with the experimental results.

**Spectroscopic Investigation of Azine (6).**—The p.e. spectrum of (6) is shown in Figure 2 and the ionization potentials are summarized in Table 2. Using Koopmans' approximation<sup>25</sup> ionization potentials are assigned to molecular orbitals. The

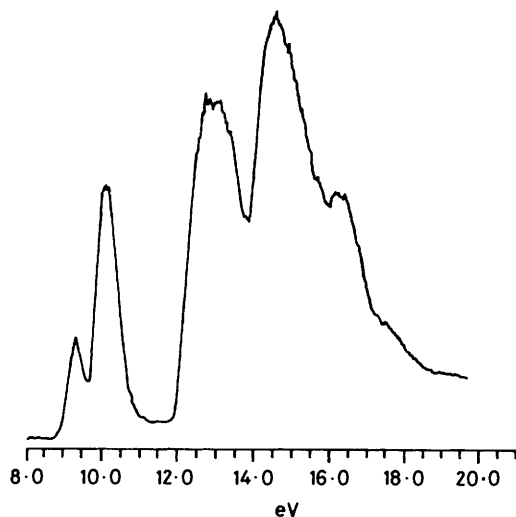


Figure 2. P.e. spectrum of azine (6)

Table 2. Vertical ionization potentials of azine (6)

IP <sub>v</sub> (eV)	Assignment
9.26	$n_N$
10.03	$\pi_{C=N}, n_O$
12.7	$\pi_{C=O}, n_N$
14.5	$\sigma, \pi_{CH_3}$
16.3	$\sigma, \pi_{CH_3}$

first band at 9.26 eV is attributed to ionization from the  $n_N^+$  (b) MO. The second band, which has a much higher intensity than the first, has to be attributed to ionizations from several MOs. Based on the MNDO results (Table 1), it is assigned to an orbital mainly of  $\pi_{C=N}$  character and to two  $n_O$  orbitals (a and b) of the two oxygen atoms. Since no shoulder at the low energy side of this band is detectable, the  $\pi_{C=N}$  (b) should be rather close to the two  $n_O$  MOs. In the conformation with  $\theta_1 = 90^\circ$  and  $\theta_2 = \theta_3 = 180^\circ$  the separation of these three MOs has a minimum value of 0.2 eV. Therefore, from the p.e. spectrum this conformation rather than that one with the lowest calculated heat of formation should be favoured, but other conformations cannot definitely be excluded. Deconvolution of this band might lead to a more conclusive result. The third band (IP<sub>v</sub> ca. 12.5 eV) is mainly due to ionizations from the  $\pi_{CO}$  orbitals.

From the  $\Delta H_f$  values calculated by the MNDO method (Table 1) one should conclude that internal rotation around the N–N bond of (6) is only slightly hindered. As a consequence, the molecule would carry out torsional motions with large amplitudes. Such unusual behaviour should be reflected also in other physical properties. For example, the i.r. spectrum should consist of very broad absorption bands, the maxima changing appreciably with the physical state of the compound.

To examine this anticipation we measured i.r. spectra of (6) in KBr, as dilute solutions in  $CCl_4$  and  $CS_2$ , and as a vapour at 75 °C. The frequencies of the strongest bands (KBr spectrum) are given in the Experimental section. All absorption bands are of ordinary width. On changing the state of aggregation only minor effects are observed. The positions of the bands are hardly shifted. For example, the carbonyl band is found at 1 699, 1 700, and 1 703  $cm^{-1}$  in KBr, solution or gas phase, respectively. Only a few weak bands are changed a little in intensity. No bands disappear and no new ones are observed. These findings are not consistent with a broad low torsional potential as suggested by

Table 3. Final positional (fractional) parameters for non-hydrogen atoms of azine (6) ( $\times 10^4$ ) (e.s.d.s in parentheses)

	x	y	z
N(1)	9 384(2)	697(2)	1 978(2)
O(1)	7 695(2)	1 756(2)	-1 733(2)
C(1)	6 910(3)	382(3)	-101(4)
C(2)	7 929(3)	1 172(2)	-508(3)
C(3)	9 275(3)	1 266(2)	626(3)
C(4)	10 328(3)	1 992(2)	142(4)

Table 4. Structure parameters of azine (6) from X-ray analysis and MNDO calculation

(a) Bond distances (pm) with e.s.d.s (in parentheses)

	X-ray	MNDO
N(1)–C(3)	128.1(3)	130.6
O(1)–C(2)	121.2(3)	122.4
C(2)–C(3)	149.7(3)	152.5
N(1)–N(1')	136.8(4)	133.9
C(2)–C(1)	147.6(4)	152.5
C(3)–C(4)	147.2(4)	150.9

(b) Valence angles (°) with e.s.d.s (in parentheses)

C(3)–N(1)–N(1')	118.0(2)	119.1
O(1)–C(2)–C(3)	119.1(2)	119.9
N(1)–C(3)–C(2)	115.0(2)	112.9
C(2)–C(3)–C(4)	119.2(2)	117.7
O(1)–C(2)–C(1)	121.4(2)	122.6
C(1)–C(2)–C(3)	119.5(2)	117.5
N(1)–C(3)–C(4)	125.8(2)	129.3

(c) Torsional angles (°) with e.s.d.s (in parentheses)

N(1')–N(1)–C(3)–C(2)	176.3(2)	175.9
N(1')–N(1)–C(3)–C(4)	-4.9(2)	-6.1
C(3)–N(1)–N(1')–C(3')	102.7(2)	149.8
O(1)–C(2)–C(3)–N(1)	173.3(2)	92.4
O(1)–C(2)–C(3)–C(4)	-5.6(2)	-85.9
C(1)–C(2)–C(3)–N(1)	-5.9(2)	-87.5
C(1)–C(2)–C(3)–C(4)	175.2(2)	146.1

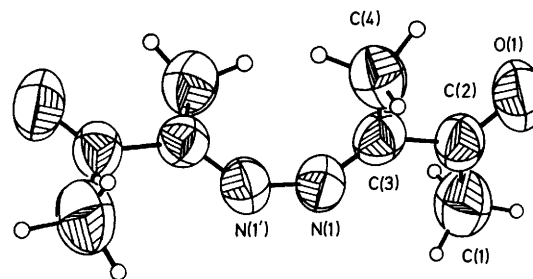


Figure 3. Molecular structure of azine (6). Thermal ellipsoids are drawn at the 50% probability level for non-hydrogen atoms

the MNDO results, but indicate the molecule to be fixed in a certain conformation.

The Raman spectrum of (6) shows no additional bands compared with the i.r. spectrum. Therefore, a centrosymmetric structure has to be excluded.

*X-Ray Structure Analysis of Azine (6).*—The atomic coordinates of azine (6) are listed in Table 3. The bond lengths and angles are given in Table 4. The numbering of the atoms is as shown in Figure 3.

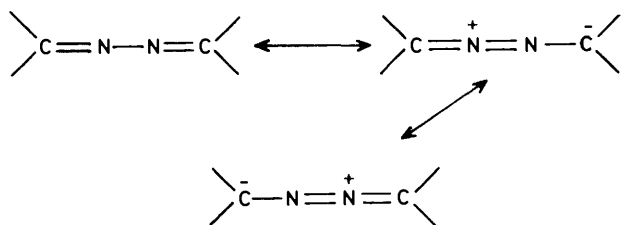
With regard to conformation the spectroscopic results as well as the expectations based on orbital interactions are confirmed by the X-ray analysis: the molecule has a *gauche* conformation; the N–N conformational angle is 102.7°. The molecule is composed of two nearly planar N=C(CH<sub>3</sub>)COCH<sub>3</sub> groups (except for the hydrogen atoms). Deviations from planarity, indicated by the torsional angles around the C=N and the C(2)–C(3) bonds, are <7°. The molecular symmetry is C<sub>2</sub>.

Obviously conjugation of the electron lone-pair of one nitrogen atom with the π system of the other half of the molecule is preferred over a completely delocalized planar octatetraene system.

This result is clearly in contrast with the MNDO calculations (Table 1), by which torsion around θ<sub>2</sub> and θ<sub>3</sub> rather than around θ<sub>1</sub> should be favoured.

Most of the observed structural parameters are in excellent agreement with the calculated ones, but there are also some deviations. In particular the torsional angles for the N–N and C(2)–C(3) bonds deviate considerably. As a consequence, also the calculated lengths for these bonds are found longer by 2.9 pm (N–N) and shorter by 2.8 pm [C(2)–C(3)], respectively. These discrepancies lead to the conclusion that interactions between n<sub>N</sub> and π<sub>C=N</sub> orbitals of the different halves of the molecule are underestimated by the MNDO method.

It is appropriate to compare the structural parameters of (6) with those of similar molecules, especially with (1),<sup>8</sup> (2),<sup>9</sup> and (5)<sup>10</sup> which have been analysed by electron diffraction. The N–N bond of (6) (136.4 pm) is shorter than that in these molecules, of which only (5) has the *gauche* conformation: (1) 141.8, (2) 143.7, and (5) 138.1 pm. There seems to be a shortening of the N–N bond on going from *anti* to *gauche*. Donor substituents on the sp<sup>2</sup> carbon atom as in (2) lengthen this bond, while it is shortened by acceptor groups as in (6). These findings can be associated with the repulsive interaction of the electron lone-pairs on the nitrogen atoms in the planar *anti* conformation. On the other hand, in the *gauche* conformation the N–N bond is strengthened by n–π conjugation (Scheme).



Scheme.

The length of the N=C double bond should show the opposite effect to substitution as the N–N bond. This is confirmed, although only to a minor extent, by the following data: (1) 127.7, (2) 127.7, (5) 126.6, and (6) 128.1 pm. The C=O bond of (6) (121.2 pm) has the same length as in related conjugated molecules like acrolein (121.4 pm) and glyoxal (121.2 pm).<sup>5</sup>

The length of the C(2)–C(3) bond is of special interest. The value of 149.7 pm is clearly greater than the standard bond distance between two sp<sup>2</sup> hybridized carbon atoms (146.6 pm). The central C–C bond in buta-1,3-diene,<sup>5</sup> acrolein,<sup>5</sup> glyoxal,<sup>5</sup> and diacetyl<sup>26</sup> has a length of 146.5, 148.4, 152.6, and 150.7 pm, respectively. The value found for (6) is between those of acrolein and glyoxal, which seems to be reasonable. The C–C bonds of the two methyl groups, C(1)–C(2) 147.6 and C(3)–C(4) 147.2 pm, seem to be rather short for single bonds between an sp<sup>2</sup> and an sp<sup>3</sup> carbon atom (standard value 151.0 pm). The shortening could at least in part be a consequence of strong hyper

conjugation between the methyl groups and the adjacent double bonds.

## Experimental

**General.**—The p.e. spectrum was recorded at ca. 50 °C on a Leybold–Heraeus UPG200 spectrometer with a He<sup>I</sup> lamp (21.21 eV) as radiation source. The spectrum was calibrated using the known ionization potentials of xenon and argon. Resolution was ca. 30 meV. N.m.r. spectra were run on a Varian XL200 spectrometer with tetramethylsilane (<sup>1</sup>H) or CDCl<sub>3</sub> (<sup>13</sup>C, δ<sub>C</sub> 77.0 p.p.m.) as internal standard. For mass spectra a Finnigan MAT312 and for i.r. spectra a Perkin-Elmer 580 instrument were used. Raman spectra were measured with a Ramanor HG2S instrument (Jobin-Yvon) (Spectra Physics argon laser). The elemental analysis was carried out on a Heraeus EA301 C, H, N analyser.

**Synthesis of 2,5-Diacetyl-3,4-diazahexa-2,4-diene (6).**—Azine (6) was prepared from diacetyl and hydrazine hydrate as described in ref. 27 and recrystallized twice from n-hexane, yield 48%, m.p. 39 °C (Found: C, 57.0; H, 7.0; N, 16.6. C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> requires C, 57.1; H, 7.2; N, 16.7%); ν<sub>max</sub>(KBr) 1 699 (CO), 1 611 (C=N), 1 360, 1 298, 1 122, and 638 cm<sup>-1</sup>; δ<sub>H</sub> (200 MHz; CDCl<sub>3</sub>) 1.35 (6 H, s, C-Me) and 1.97 (6 H, s, CO-Me); δ<sub>C</sub> (50.3 MHz; CDCl<sub>3</sub>) 10.7 (q, C-Me), 23.9 (q, CO-Me), 151.6 (s, C=N), and 196.2 p.p.m. (s, C=O); m/z 168 (3%, M<sup>+</sup>), 125 (19, M<sup>+</sup> – COMe), and 43 (100, COMe<sup>+</sup>).

**X-Ray Structure Analysis.**—Crystal data. C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>, M = 168.20. Monoclinic, a = 9.876(4), b = 12.428(4), c = 7.986(2) Å, β = 98.59(3)°, V = 969.2(6) Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group C2/c (No. 15), Z = 4, D<sub>x</sub> = 1.15 g cm<sup>-3</sup>. Pale yellow needles. Crystal dimensions: 0.78 × 0.46 × 0.31 mm, μ(Mo-K<sub>α</sub>) = 0.79 cm<sup>-1</sup>.

**Data collection and processing.** Syntex R3 four-circle diffractometer, 2θ–ω scan mode, 2θ<sub>max</sub> = 60°, ω scan speed 3.0–30.0 deg min<sup>-1</sup>, graphite-monochromated Mo-K<sub>α</sub> radiation; 1 220 independent reflections measured giving 657 with F<sub>0</sub> ≥ 4.5σ(F<sub>0</sub>).

**Structure analysis and refinement.** The co-ordinates of all non-hydrogen atoms were determined by direct methods and refined using the SHELXTL program system<sup>28</sup> on a Data General NOVA 3/12 computer. The positions of the hydrogen atoms were calculated on ideal geometry and refined as rigid groups (C–H distance 96 pm, H–C–H angle 109.5°). The isotropic temperature factors were given the 1.2 fold of the U<sub>ij</sub> tensor of the corresponding C atom. The refinement converged to R = 0.059, R<sub>w</sub> = 0.067, weighting scheme w<sup>-1</sup> = σ<sup>2</sup>(F) + 4.6 × 10<sup>-4</sup>F<sup>2</sup>. Residual electron density 0.17 e/Å<sup>3</sup>.

## Acknowledgements

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