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# Self-Complementary Hydrogen Bonding of 1,1'-Bicyclohexylidene-4,4'-dione Dioxime. Formation of a Non-Covalent Polymer.

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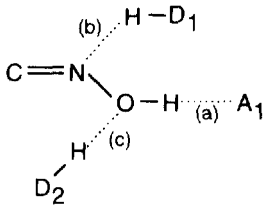
***Abstract:*** 1,1'-Bicyclohexylidene-4,4'-dione dioxime **2** self-assembles into a non-covalent polymer structure in the solid state due to intermolecular directional hydrogen bonding between the oxime functionalities.

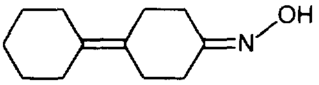
## INTRODUCTION

The design of novel solid state structures based on non-covalent interactions is explored extensively.[1] Strong (hydrogen bonding, metal-ligand)[2] and weak (Van der Waals, π-π (arene-arene) and weak C-H···Y hydrogen bonding)[3] intermolecular interactions have been used for molecular recognition induced association of (self)-complementary units.[4] Especially hydrogen bonding is attractive since hydrogen bonds are moderately strong (1 - 5 kcal/mol) and possess directionality. Structures with one- (stacks, tapes, ribbons, chains), two- (layers, sheets)[5] and three-dimensional ('diamondoid')[6] motifs have been prepared.

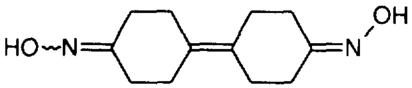
Among the group of hydrogen bond donors and -acceptors, the oxime functionality has hitherto received little attention despite the fact that its hydrogen bonding modes are well documented.[7,8] Three types of intermolecular hydrogen bond formation have been identified: (a) O-H···$A_1$, (b) N···H-$D_1$, (c) O···H-$D_2$. In all cases the oxime group possesses an *anti periplanar* conformation.



Recently, we have reported on the synthesis of (end-functionalized) oligo(cyclohexylidenes) for application as novel molecular building blocks. These molecules consist of cyclohexane units linked at the 1,4-positions *via* double bonds.[9] Single-crystal X-ray structures of several derivatives revealed a highly ordered, regular rodlike structure in which the cyclohexyl-type rings adopt a chair conformation.[9,10] Hence, we anticipated that by functionalization with groups suitable for directional hydrogen bonding new self-complementary molecular building blocks will be accessible. Here we show that cyclohexylidene oximes **1** and **2** fullfil this goal.



**1**



**2**

## RESULTS AND DISCUSSION

Compounds **1** and **2** were synthesized (yield: **1** 89% and **2** 53%) from the corresponding ketones by treatment with hydroxylamine hydrochloride in the presence of pyridine as a base (see Experimental Section). Compound **1** was obtained as a crystalline white solid which is readily soluble in both polar and apolar organic solvents. Two endotherms were discernible in its Differential Scanning Calorimetry (DSC) curve: a solid-solid transition at 83 °C (ΔH -0.38 kcal/mol) and a melting peak at 114 °C (ΔH -4.62 kcal/mol).

Recrystallization from benzene afforded crystals suitable for single-crystal X-ray analysis. Oxime **1** crystallizes in the space group $P\bar{1}$ and the unit cell contains two crystallographic independent molecules (**1**(***n***); ***n*** = 1 and 2) which are joined to their symmetry-related molecules *via* two hydrogen bonds of the type O-H···N (type (a)) and N···H-O (type (b)), respectively (*vide supra*). The oxime group of both **1**(*1*) and **1**(*2*) is disordered over two positions, related by a 180° rotation around the C=N bond (disorder ratio for both **1**(*1*) and **1**(*2*) 0.53 : 0.47). The dimers possess a rodike structure with the cyclohexyl rings adopting a chairlike conformation (Fig. 1a). The crystallographic independent dimers are packed in an alternating fashion in the solid state which results in the high packing coefficient[11] of 72.6%. Columns parallel to the *b* axis and layers in the *ab* plane are formed (Fig. 1b). In Table 1 selected bond lengths and valence angles of **1**(*1*) and **1**(*2*) are presented; all values are in line with expectation.

Table 1. Selected Bond Lengths (Å) and Valence Angles (°) for **1**(***n***); ***n*** = 1 and 2 (Esd's in Parentheses).

| bond | bond length | | angle | valence angle | |
|---|---|---|---|---|---|
| | ***n*** = 1 | ***n*** = 2 | | ***n*** = 1 | ***n*** = 2 |
| C(*n*4)-C(*n*7) | 1.338(3) | 1.344(4) | N(*n*)-C(*n*1)-C(*n*2) | 121.5(3) | 120.2(3) |
| C(*n*1)-N(*n*) | 1.277(3) | 1.278(3) | N(*n*)-C(*n*1)-C(*n*6) | 119.5(3) | 123.2(3) |
| N(*n*)-O(*n*)[a] | 1.487(5) | 1.468(4) | C(*n*2)-C(*n*1)-C(*n*6) | 118.8(2) | 116.5(2) |
| N(*n*)-O(*n*)[b] | 1.495(5) | 1.509(7) | C(*n*1)-N(*n*)-O(*n*)[a] | 114.2(3) | 113.5(3) |
| C(*n*1)-C(*n*6) | 1.497(4) | 1.485(4) | C(*n*1)-N(*n*)-O(*n*)[b] | 114.0(3) | 115.3(3) |
| C(*n*1)-C(*n*2) | 1.496(4) | 1.496(4) | | | |

(a) Major disorder component. (b) Minor disorder component.

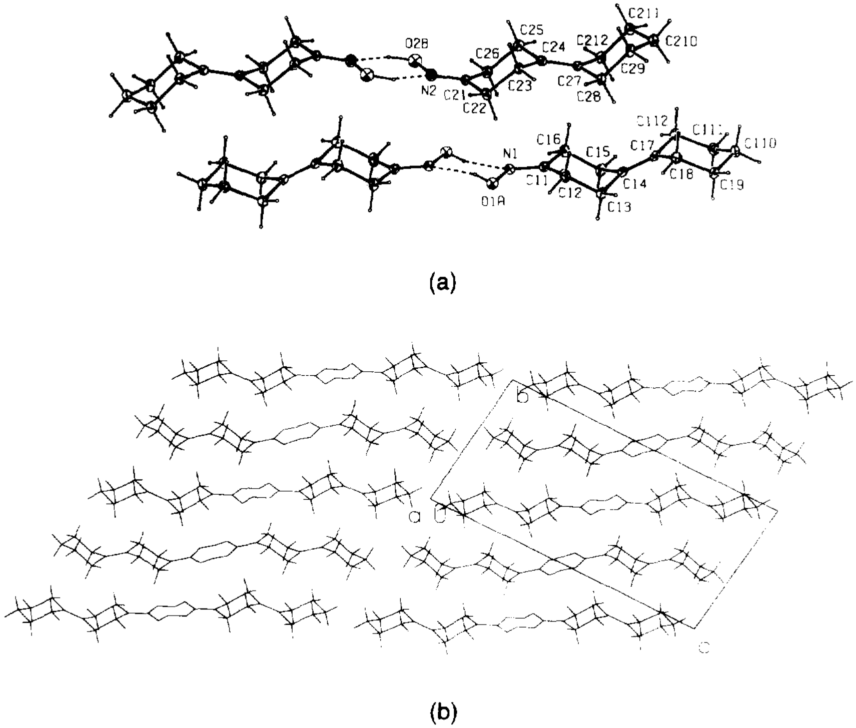


Fig. 1. ORTEP[12] (30% probability level) representation of dimers of **1**(*1*) and **1**(*2*). Only the major disorder components are shown (a). Crystal packing of **1** viewed along the *a* axis (b).

The two hydrogen bonds in the dimer give a six-membered central ring which possesses a nearly planar conformation except for the major component of molecule **1**(*1*) where it adopts a chair-like conformation (Fig.1a). The hydrogen bond donor-acceptor distance (D···A; range 2.707-2.750 Å) is significantly smaller than the sum of the isotropic Van der Waals radii (N, 1.55 Å; O, 1.52 Å)[13] and is shorter than the average value (2.822 Å) found for other oxime dimers.[8] The D-H···A hydrogen bond angles (range 145-166°) do not deviate much from linearity (Table 2).[14]

Table 2. Hydrogen Bond Lengths (Å) and Angles (°) for **1**(***n***) (Esd's in Parentheses).

| molecule | disorder | Donor-Acceptor | D···A | D-H | H···A | D-H···A |
|---|---|---|---|---|---|---|
| **1**(*1*) | a | O(1)-H(1)···N(1)$^{I\,c}$ | 2.739(4) | 0.736(4) | 2.076(3) | 150.2(4) |
| | b | O(1)-H(1)···N(1)$^{I\,c}$ | 2.707(4) | 1.110(5) | 1.718(4) | 145.6(3) |
| **1**(*2*) | a | O(2)-H(2)···N(2)$^{II\,c}$ | 2.750(4) | 1.043(4) | 1.767(4) | 155.3(2) |
| | b | O(2)-H(2)···N(2)$^{II\,c}$ | 2.743(6) | 0.813(6) | 1.947(3) | 166.3(5) |

(a) Major disorder component. (b) Minor disorder component. (c) Symmetry codes: (I) 1 - x, 1 - y, 1 - z; (II) 1 - x, 2 - y, 1 - z.

It should be stipulated that both the lower homologue of **1**, *i.e.* cyclohexanone oxime (**3**)[15], and the model compound acetoxime (**4**)[16] possess packing motifs in which *trimeric*, instead of *dimeric*, species are formed *via* intermolecular hydrogen bonding.

Solid state IR analysis supports the hydrogen bonded structure of **1**. The absorption pattern in the region 3350-3100 cm$^{-1}$ is indicative for the presence of strongly hydrogen bonded OH groups.[17] Furthermore an O-H out-of-plane vibration at 756 cm$^{-1}$ is found, of which the assignment has been established by deuteration experiments. In dilute $CCl_4$ solution an equilibrium between the monomeric and dimeric form of **1** exists as shown by the presence of an additional sharp peak a 3605 cm$^{-1}$ (free OH).

Concomitant with the introduction of a second oxime functionality in going from **1** to **2** significant changes in physical properties are found. Dioxime **2** is virtually insoluble in organic solvents, with the exception of polar aprotic ones (*vide infra*), and, in contrast to **1**, no clear melting point was observed. DSC and Thermal Gravimetrical Analysis (TGA; $N_2$ atmosphere) show that decomposition of **2** sets in at 220 °C whereas **1** sublimes at 125 °C. These results suggest a strongly self-associated solid state structure for **2**. This is supported by both the IR and Raman data of **2**. No absorptions above 3350 cm$^{-1}$ are discernible, hence, the presence of free OH groups can be ruled out. The occurrence of extensive hydrogen bonding is further corroborated by the O-H out-of-plane vibration situated at 757 cm$^{-1}$ (IR). In the case of **1** it is positioned at 756 cm$^{-1}$ whereas for **3** and **4**, which both possess a trimeric hydrogen bonded structure,[15,16] the O-H out-of-plane vibration is found at 795 cm$^{-1}$ and 800 cm$^{-1}$, respectively. Since the O-H out-of-plane vibration is very sensitive to the mode of intermolecular association,[18] we conclude that the type of hydrogen bonding for **2** has to be identical to that of **1**, *i.e.* the oxime groups participate in hydrogen bonding by forming six-membered rings.

It should be pointed out that according to $^{13}$C NMR spectroscopy two isomers of **2** are present, *i.e.* **2(*syn*)** and **2(*anti*)**. For each isomer six resonances (2 olefinic and 4 aliphatic) are anticipated. In the $^{13}$C NMR spectrum of **2** two sets of 6 resonances with equal intensities are found, indicative of a *ca.* 1:1 molar ratio (Fig. 2a). Despite the presence of **2(*syn*)** and **2(*anti*)** only one C=N absorption is found in the IR spectrum (1676 cm$^{-1}$) and one C=C absorption in the Raman spectrum (1666 cm$^{-1}$).

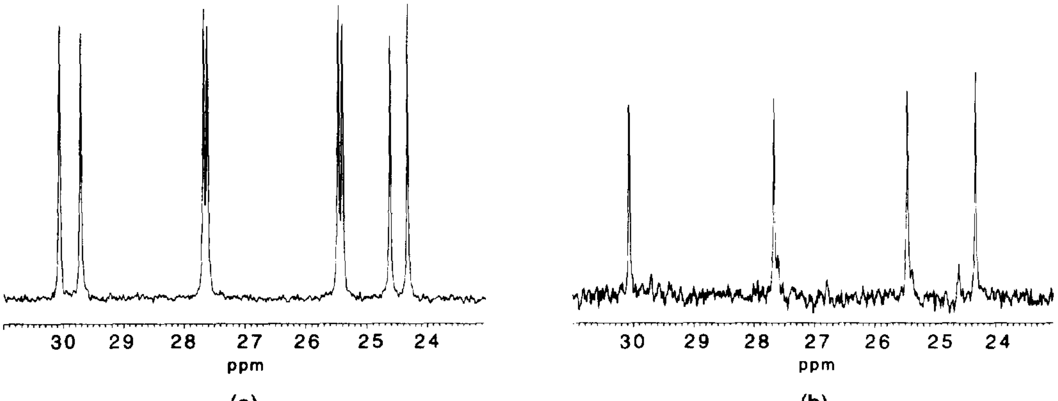


Fig. 2. Aliphatic part of the $^{13}$C NMR spectrum (DMSO-$d_6$, 298 K) of **2** (**2(*syn*)**:**2(*anti*)** *ca.* 1:1) (a) and pure **2(*anti*)** (b).

These results, in combination with the X-ray and spectroscopic data reported for **1**, strongly suggest a non-covalent polymer structure for **2**. Three types of non-covalent polymers can be envisaged due to the availability of **2(*syn*)** and **2(*anti*)** (Fig. 3). Although we cannot distinguish between these possibilities on the basis of the IR and Raman data, we feel that the random *syn-anti* polymer is most likely.

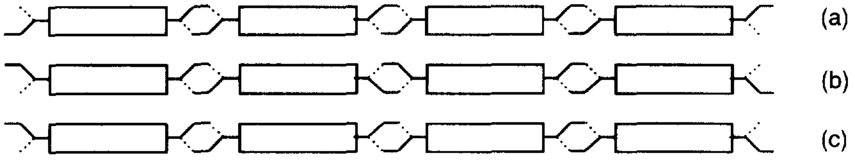


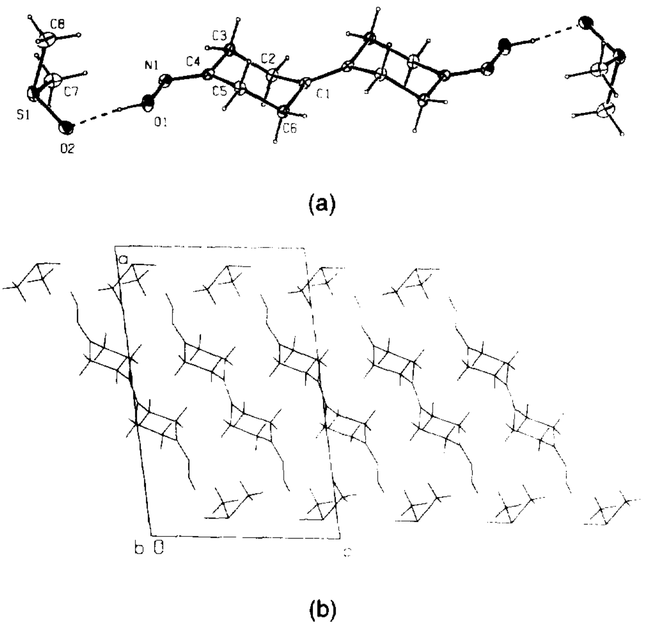
Fig. 3. Schematic representation of the possible polymer structures for dioxime **2**: all-*anti* (a), all-*syn* (b) and random *syn-anti* (c).

In line with the proposed polymer structure an increase in density is found in going from **1** ($D_{calc}$ 1.204 g cm$^{-3}$, see Experimental Section) to **2** (1.63 g cm$^{-3}$ (298 K, picnometry)). The lower homologue 1,4-cyclohexanedione dioxime (**5**) possesses a solid state packing motif in which each molecule is linked to four other molecules *via* intermolecular hydrogen bonding, giving an infinite double chain pattern.[19] The density of **2** is significantly higher than that of **5** (1.35 g cm$^{-3}$)[19] and 1,5-cyclooctanedione dioxime (**6**, 1.228 g cm$^{-3}$).[20] Despite the presence of two oxime functionalities in **6**, it crystallizes in a trimeric structure. This indicates that hydrogen bonding in dioximes is strongly affected by the molecular geometry of the hydrocarbon part of the molecule. In our case the presence of the semirigid, extended bicyclohexylidene framework enables the efficient solid state packing of **2**.

Wide angle X-ray powder diffraction (WAXD) measurements confirmed the crystalline nature of **2** (see Experimental Section). The definite answer concerning the solid state structure of **2** should come from a single-crystal X-ray structure determination. Due to its insolubility in all organic solvents except polar aprotic ones, suitable crystals could only be obtained from a DMSO/$C_6H_6$ mixture. Single-crystal X-ray analysis revealed that co-crystals containing one molecule of **2** and two molecules of DMSO were obtained (space group $P2_1/c$ with the unit cell containing two molecules of **2+2DMSO**). Instead of intermolecular hydrogen bonding to other oxime groups, hydrogen bonds are formed with the oxygen atom of DMSO. Moreover, only the *anti* isomer is present! This can be rationalized by the observation that **2(*anti*)** has no net dipole moment whereas **2(*syn*)** does have a net dipole moment. As a consequence, **2(*syn*)** will be stabilized by solute-solvent interactions relatively to **2(*anti*)**.[21]

The chair-chair structure of the bicyclohexylidene skeleton is comparable to that of **1** while hydrogen bonding with a high degree of linearity is now of the type O-H···O=S (hydrogen bond lengths and angle: O(1)···O(2) 2.6529(17) Å; O(1)-H(1) 0.89(2) Å; H(1)···O(2) 1.77(2) Å; O(1)-H(1)···O(2) 172.(2)°) (Fig. 4 and Table 3).

As mentioned previously, the $^{13}C$ NMR spectrum of crude **2** contains signals attributable to **2(*syn*)** and **2(*anti*)**. The $^{13}C$ NMR spectrum of the co-crystals **2+2DMSO** only showed one set of signals (Fig. 2b), while the $^{13}C$ NMR spectrum of the mother liquor contained the resonances assigned to **2(*syn*)** with considerably increased intensity. An estimate of the barrier for oxime nitrogen inversion ($\Delta H^{\ddagger}$) was obtained for **1** and **3** using semiempirical AM1 calculations (see Experimental Section). The $\Delta H^{\ddagger}$ values, 46.4 and 46.3 kcal/mol, respectively, are in excellent agreement with previously reported theoretical values obtained for other derivatives.[22] Since an inversion process would render the sets of carbon resonances of **2**(*anti*) and **2**(*syn*) identical, high temperature $^{13}C$ NMR measurements (DMSO-$d_6$) were performed. In line with the calculated activation enthalpies, no coalescence of signals was observed upon heating within the highest accessible temperature (423 K), indicating that the inversion process at the nitrogen atoms is indeed very slow on the NMR timescale. Nevertheless, keeping a solution of **2**(*anti*) in DMSO at 373 K for 72 hours gradually gave a $^{13}C$ NMR spectrum identical to that of the starting material, *i.e.* a 1:1 molar mixture of isomers.



(a)

(b)

Fig. 4. ORTEP[12] (30% probability level) representation of **2+2DMSO** (a). Crystal packing of **2+2DMSO** viewed along the *b* axis (b).

Table 3. Selected Bond Lengths (Å) and Valence Angles (°) for **2+2DMSO** (Esd's in Parentheses).

| bond | bond length | angle | valence angle |
|---|---|---|---|
| C(1)-C(1a) | 1.340 (2) | N(1)-C(4)-C(3) | 116.10(12) |
| N(1)-C(4) | 1.2803(19) | N(1)-C(4)-C(5) | 127.10(13) |
| N(1)-O(1) | 1.4090(18) | C(3)-C(4)-C(5) | 116.80(12) |
| C(3)-C(4) | 1.4956(19) | O(1)-N(1)-C(4) | 112.69(11) |
| C(4)-C(5) | 1.4982(18) | N(1)-O(1)-H(1) | 98.9 (15) |
| S(1)-O(2) | 1.5069(13) | | |

In passing we like to remark that in going from 1,4-cyclohexanedione (**7**) to 1,4-cyclohexanedione dioxime (**5**) the conformation of the cyclohexane-type ring remains almost unaffected: twist-boat conformers are found.[19] This changes dramatically in the case of 1,1'-bicyclohexylidene-4,4'-dione (**8**) and its dioxime **2**. In Fig. 5 the single-crystal X-ray structure of dione **8** is shown. Two crystallographic independent molecules, one of which is located at a center of symmetry, are found. Therefore, there are three independent hexanone moieties in the asymmetric unit, two of which display disorder in the six-membered ring, resulting in both chair and (twist) boat conformations for the six-membered rings of **8**.[23]

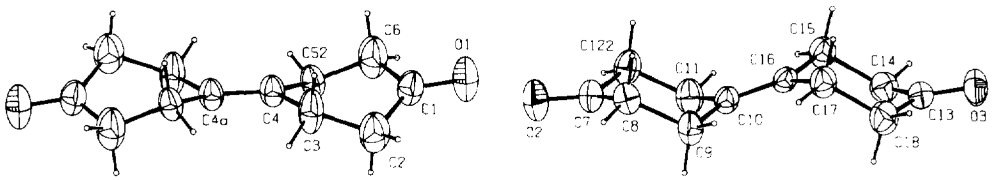


Fig. 5. ORTEP[12] (30% probability level) representation of **8**. Only the major disorder components are shown.

Although we cannot fully exclude that the presence of DMSO in the case of the **2+2DMSO** co-crystals affects the molecular geometry of **2**, these results suggest that the introduction of oxime functionalities significantly modifies the conformational preferences of the bicyclohexylidene skeleton in the solid state.

## CONCLUSION

A non-covalent polymer structure for dioxime **2** in the solid state is proposed on the basis of its thermal behaviour, solubility properties, IR and Raman data, density and structural resemblance to **1**. Our results point to the application of oximes as functionalities for novel self-assembling systems.

## EXPERIMENTAL SECTION

All reactions were carried out under a dry $N_2$ atmosphere. Ethanol was stored on 4 Å molecular sieves. NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300 MHz for $^1H$ NMR and 75 MHz for $^{13}C$ NMR. Chemical shifts are given relative to external TMS. Infrared spectra were recorded on a Mattson RS spectrophotometer applying the KBr pelletting technique for solids. Solution spectra were recorded in $CCl_4$ in 1 mm NaCl cells. Raman spectra were recorded on a Perkin Elmer 2000 FT-NIR-Raman spectrophotometer. Differential scanning calorimetry was done using a Mettler DSC 12E with samples (1-2 mg) in sealed aluminium pans (heating and cooling rate 5 °C/min). Thermogravimetry was performed on a Perkin Elmer TGS-2 Thermogravimetric System under an $N_2$ atmosphere: heating rate 20 °C/min. The density of crude **2** was determined in triplicate using picnometry[25] (picnometer volume 10 mL, solvent *n*-decane, T = 25.3 ± 0.1 °C). Wide Angle X-Ray Diffraction (WAXD) patterns were obtained at ambient temperature using a Delft Instruments Guinier Johansson FR552 camera at a wavelength of 1.5405 Å. Elemental analyses were carried out by H. Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

**1,1'-Bicyclohexyliden-4-one oxime (1).** To a solution of 1,1'-bicyclohexyliden-4-one[9] (5.00 g, 28.1 mmol) in ethanol (100 mL) was added pyridine (2.22 g, 28.1 mmol) and hydroxylamine hydrochloride (2.97 g, 42.2 mmol). The resulting solution was refluxed overnight and after cooling to room temperature the solvent was removed under reduced pressure. To the resulting brownish solid a saturated $K_2CO_3$ solution (100 mL) was added and the organic material was extracted using chloroform (5 × 50 mL). After drying ($MgSO_4$) and solvent removal *in vacuo* a white solid was obtained (4.82 g, 25.0 mmol, 89%), mp 114 °C. $^1$H NMR ($C_6D_6$) 8.76 (s, 1 H), 2.60 (m, 2 H), 2.26 (m, 2 H), 2.12 (m, 4 H), 1.98 (m, 4 H), 1.40 (m, 6 H); $^{13}$C NMR ($C_6D_6$) 159.90, 132.18, 125.66, 31.06, 30.47, 30.39, 28.69, 28.41, 27.98, 27.32, 25.87, 25.77; IR (KBr) 3255, 3167, 2983, 2965, 2958, 2850, 2844, 2828, 1677, 1457, 1447, 1435, 1426, 993, 974, 927, 920, 756; Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25; O, 8.27. Found: C, 74.38; H, 10.05; N, 7.23; O, 8.21.

**1,1'-Bicyclohexylidene-4,4'-dione dioxime (2).** To a solution of 1,1'-bicyclohexylidene-4,4'-dione **8**[9] (1.63 g, 8.49 mmol) in ethanol (50 mL) was added pyridine (1.34 g, 16.9 mmol) and hydroxylamine hydrochloride (1.77 g, 25.4 mmol). The resulting suspension was refluxed overnight and after cooling to room temperature an off white powder precipitated which was filtered off (1.00 g, 4.50 mmol, 53%). $^1$H NMR (mixture of isomers; DMSO-$d_6$) 10.16 (s, 2 H), 2.38 (m, 4 H), 2.31 (m, 4 H), 2.26 (m, 8 H); $^{13}$C NMR (DMSO-$d_6$) **2(*anti*)** 157.04, 128.09, 30.04, 27.64, 25.44, 24.30; $^{13}$C NMR (DMSO-$d_6$) **2(*syn*)** 157.10, 128.12, 29.68, 27.58, 25.37, 24.58; **IR (KBr)** 3227, 3178, 3129, 2984, 2959, 2845, 1676, 1478, 1440, 1425, 1204, 981, 955, 911, 757; Anal. Calcd for $C_{12}H_{18}N_2O_2$: C, 64.84; H, 8.16; N, 12.60; O, 14.40. Found: C, 64.66; H, 8.11; N, 12.51; O, 14.34. WAXD (2θ): 14.35, 15.10, 16.60, 17.70, 19.25, 23.40, 25.25, 25.60, 26.45, 29.00, 31.50, 33.00, 35.65, 39.60.

**Calculations.** Calculations were performed with the AM1 Hamiltonian[26] as implemented in MOPAC 6.0 (PC version).[27] Geometry optimization was executed without imposing any constraints using the keyword PRECISE. Minima and transition states were characterized by a Hessian calculation (keywords FORCE, LARGE); either none or only one imaginary vibration, respectively, was found. Calculations were performed on a 486/33 MHz personal computer.

**X-ray structure determination of 1, 2+2DMSO and 8.**[28] Crystals suitable for X-ray structure determination were mounted on a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD4-Turbo diffractometer on rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 25 well-centered reflections (SET4) in the range 8.92° < θ < 15.02°, 10.14° < θ < 15.45°, and 8.60° < θ < 14.96° for **1**, **2+2DMSO** and **8**, respectively. The unit-cell parameters were checked for the presence of higher lattice symmetry.[29] Crystal data and details on data collection are collected in Table 4. Data were corrected for *Lp* effects and for the observed linear decay of the reference reflections. For compound **8** the standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections:$\sigma^2(I) = \sigma_{cs}^2(I) = (0.01I)^2$.[30] No absorption correction was applied. All structures were solved by automated direct methods (SHELXS86[31] for **1** and **2+2DMSO**; SIR-92[32] for **8**). Compounds **1** and **2+2DMSO** were refined on $F^2$ by full-matrix least-squares techniques (SHELXL-93[33]); no observance criteria were applied during refinement. Refinement on $F$ was carried out by

Table 4. Crystallographic Data for **1**, **2+2DMSO** and **8**.

| complex | **1** | **2+2DMSO** | **8** |
|---|---|---|---|
| *Crystal data* | | | |
| Formula | $C_{12}H_{19}NO$ | $C_{12}H_{18}N_2O_2.2C_2H_6OS$ | $C_{12}H_{16}O_2$ |
| Molecular weight | 193.29 | 378.56 | 192.26 |
| Crystal system | triclinic | monoclinic | monoclinic |
| Space group | $P\ \bar{1}$ (No. 2) | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) |
| $a$, Å | 6.1699(3) | 15.5775(8) | 5.3217(3) |
| $b$, Å | 9.6920(7) | 6.1047(4) | 25.5026(11) |
| $c$, Å | 18.8634(9) | 10.0725(12) | 12.3697(6) |
| $\alpha$, deg | 81.146(6) | - | - |
| $\beta$, deg | 88.007(4) | 97.838(7) | 109.244(5) |
| $\gamma$, deg | 73.001(6) | - | - |
| V, Å$^3$ | 1065.81(11) | 948.91(14) | 1584.98(14) |
| $D_{calc}$, g cm$^{-3}$ | 1.204 | 1.325 | 1.209 |
| $Z$ | 4 | 2 | 6 |
| $F$(000) | 424 | 408 | 624 |
| $\mu$, cm$^{-1}$ | 0.7 | 3.0 | 0.8 |
| Crystal size, mm | 0.13 × 0.38 × 0.50 | 0.28 × 0.48 × 0.70 | 0.1 × 0.1 × 0.6 |
| *Data collection* | | | |
| $T$, K | 150 | 150 | 298 |
| $\theta_{min}$, $\theta_{max}$ deg | 1.1, 27.5 | 1.3, 27.5 | 1.0, 24.2 |
| Wavelength (Mo K$\alpha$, graphite monochr.), Å | 0.71073 | 0.71073 | 0.71073 |
| Scan type | $\omega/2\theta$ | $\omega/2\theta$ | $\omega/2\theta$ |
| $\Delta\omega$, deg | $0.73 + 0.35\tan\theta$ | $0.54 + 0.35\tan\theta$ | $0.61 + 0.35\tan\theta$ |
| Hor., ver. aperture, mm | 3.17, 4.00 | 3.00, 4.00 | 3.00, 4.00 |
| X-ray exposure time, h | 20 | 11 | 16 |
| Linear decay, % | 2 | 2 | < 1 |
| Reference reflections | $\bar{2}\ 0\ 3,\ \bar{1}\ \bar{2}\ 4,\ \bar{1}\ \bar{4}\ 2$ | $\bar{4}\ 2\ \bar{2},\ 5\ 2\ \bar{2},\ 2\ 2\ \bar{4}$ | $\bar{2}\ 0\ 2,\ 0\ 2\ \bar{6},\ 0\ 9\ 2$ |
| Data set | -8 : 6, -12 : 12, -24 : 24 | -20 :20, 0 : 7, -13 : 13 | -6 : 0, -29 : 0, -13 : 13 |
| Total data | 7775 | 5020 | 2920 |
| Total unique data | 4870 | 2172 | 2526 |
| Observed data | [no obs. crit. applied] | [no obs. crit. applied] | 1222 [$I > 2.5\sigma(I)$] |
| *Refinement* | | | |
| No. of refined params. | 255 | 114 | 212 |
| Final $R$ $^a$ | 0.074 [2239 $I > 2\sigma(I)$] | 0.037 [1817 $I > 2\sigma(I)$] | 0.047 |
| Final $wR2$ $^b$ | 0.185 | 0.099 | - |
| Final $R_w$ $^c$ | - | - | 0.055 |
| Goodness of Fit | 0.96 | 1.07 | 0.68 |
| $w^{-1}$ $^d$ | $\sigma^2(F^2) + (0.0699P)^2$ | $\sigma^2(F^2) + (0.0494P)^2 + 0.24P$ | $\sigma^2(F)$ |
| $(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$ | 0.000, 0.000 | 0.000, 0.000 | 0.013, 0.119 |
| Min. and max. residual density, e Å$^{-3}$ | -0.31, 0.35 | -0.42, 0.36 | -0.18, 0.18 |

(a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ (b) $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

(c) $R_w = [\Sigma[w(||F_o| - |F_c||)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ (d) $P = (\text{Max}\ (F_o^2, 0) + 2F_c^2)/3$

full-matrix least-squares techniques (SHELX76[34]) for compound **8**. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms, except for the oxime hydrogen atom of **2+2DMSO**, which was located on a difference Fourier map and subsequently included in the refinement, and the oxime hydrogen atoms of **1** which were included at fixed positions. The DMSO methyl group of **2+2DMSO** was refined as a rigid group allowing for rotation around the S-C bond. Compound **1** displays disorder in the oxime moiety whereas compound **8** displays disorder in the ring systems. For both compounds a disorder model was introduced. Non-hydrogen atoms were refined with anisotropic thermal parameters, except for the disordered oxygen of **1**. The hydrogen atoms of **1** and **2+2DMSO** were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic parameter of their carrier atoms by a factor of 1.5 for the methyl and oxime hydrogens and a factor of 1.2 for the other hydrogen atoms, respectively. The hydrogen atoms of **8** were refined with two overall isotropic thermal parameters with values of 0.096(4) and 0.149(9) $Å^2$ for the disordered hydrogen atoms and the other hydrogen atoms, respectively. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography[35] for **1** and **2+2DMSO**. Compound **8** was refined using neutral atom scattering factors taken from Cromer and Mann[36], amplified with anomalous-dispersion corrections from Cromer and Liberman.[37] Geometrical calculations and illustrations were performed with PLATON[12]; all calculations were performed on a DECstation 5000 cluster.

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23. The minor component (site occupation factor 0.39) of the disordered six-membered ring containing C(1) possesses a slightly distorted chair conformation (all relevant asymmetry parameters[24] are less then 15°). The major component of this ring system is intermediate between a boat ($\Delta C_s$[C(2)] = 18.0(8)°, $\Delta C_s$[C(3) - C(4)] = 13.0(9)°) and a twist-boat conformation ($\Delta C_2$[C(1)] = 20.4(7)°, $\Delta C_2$[C(2) - C(3)] = 24.8(9)°). The major component (site occupation factor 0.62) of the six-membered ring containing C(7) is in an ideal (as far as the $sp^2$ hybridization of C(7) and C(10) allows) chair conformation, with all relevant asymmetry parameters less then 1.3°; wheras the minor component displays a boat conformation ($\Delta C_s$[C(9)] = 1.7(6)°, $\Delta C_s$[C(7) - C(8)] = 1.4(9)°). The ordered six-membered ring containing C(13) is in a chair conformation with all relevant asymmetry parameters less then 9.0°. Selected bond lengths (Å): C(4)-C(4a) 1.296(5); C(10)-C(16) 1.329(5); C(1)-O(1) 1.203(6); O(2)-C(7) 1.191(6); O(3)-C(13) 1.202(5).
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28. Atomic coordinates (including calculated H atom coordinates), thermal parameters, bond lengths and valence angles for the crystal structure determination of compounds **1**, **2+2DMSO** and **8** have been

deposited at the Cambridge Crystallographic Data Centre. They can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK.

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