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**X-RAY STRUCTURE AND DYNAMIC BEHAVIOUR IN SOLUTION OF
N-METHYLTHIO-N'-(2,6-DIMETHYLPHENYL)-2,6-DIMETHYL-1,4-
QUINONEDIIMINE FORMED BY THE ALCOHOLYSIS OF
[Me₂Al{2,6-Me₂C₆H₃NS(Me)NC₆H₃Me₂-2,6}]₂**

J.M. KLERKS, G. VAN KOTEN, K. VRIEZE *

*Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, J.H. van 't Hoff Instituut,
Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)*

and P. SEIGNETTE

*Laboratorium voor Kristallografie, Universiteit van Amsterdam, J.H. van 't Hoff Instituut,
Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)*

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Summary

Reaction of [Me₂Al{RNS(Me)NR}]₂ (R = 2,6-Me₂C₆H₃) with *t*-BuOH affords *N*-methylthio-*N'*-(2,6-dimethylphenyl)-2,6-dimethyl-1,4-quinonediimine in 67% yield. The X-ray structure of this compound shows that two conformational isomers are present in the solid. Temperature dependent ¹³C and ¹H NMR measurements show that in solution these conformers exchange at a rate which is fast on the NMR time scale at +60°C and slow at -60°C. From the coalescence point of two of the ¹³C resonances, the free energy of activation is estimated to be 13.7 + 1.0 kcal/mol at 10°C. Possible processes for the exchange are discussed, and also a reaction scheme for the formation of the title compound is discussed.

Introduction

Chemical activation of hetero-olefines by metal atoms has been studied in our laboratory mainly with compounds of α-diimines (RN=CHCH=NR) [1–4], sulfurdiimines (RN=S=NR) [5–7], sulfinylanilines (RN=S=O) [7,8] and sulfines R₂C=S=O [9,10]. For RNSNR and RNSO it has been shown that chemical activation and subsequent N=S bond rupture is favoured by initial η²-N=S coordination to low valent electron-rich transition metal atoms [6,7]. The RNS, S and NR fragments so formed may then be captured by formation of cluster complexes [6,7]. Chemical activation and conversion of RNSNR or

* To whom correspondence should be addressed.

RNSO may also take place by addition of organolithium, organomagnesium [11,12] or organoaluminium compounds [5] to the N=S double bond. For the sulfurdiimines this gives the $[\text{RNS}(\text{R}')\text{NR}]^-$ ligand which may be transferred to copper(I), silver(I), rhodium(I) or palladium(II) in metathesis reactions [12,13]. The resulting transition metal complexes decompose quantitatively in solution into RN=NR and SR' segments, at a rate which depends on the metal ion and the stereo and electronic properties of R and R' [12,14]. The aluminium compounds of this ligand [5] also decompose in solution, although in a less specific way. In addition to RN=NR, RNH₂ and polymeric material were also isolated from the reaction mixture [5]. Hydrolysis or alcoholysis of the transition metal complexes [7] as well as of the Al complexes [5] of the $[\text{RNS}(\text{R}')\text{NR}]^-$ ligand generally gives RNH₂ and RN=NR, and only one exception is known, viz. the reaction of $[\text{Me}_2\text{Al}\{\text{RNS}(\text{Me})\text{NR}\}]_2$ (R = 2,6-Me₂C₆H₃) with t-BuOH, which affords a sulfenylimine in high yield and in a remarkably specific way. The structure of this compound in the solid state and in solution is discussed below.

Experimental

All manipulations were carried out under dry, oxygen-free nitrogen. The very air and moisture sensitive $[\text{Me}_2\text{Al}\{\text{RNS}(\text{Me})\text{NR}\}]_2$ (R = 2,6-Me₂C₆H₃) was prepared by a published procedure [5]. Pentane was dried and purified by distillation from Na/K alloy and t-butanol by distillation from t-BuOK. The exact molecular mass was determined on a Varian MAT 711 mass spectrometer. ¹H NMR spectra were recorded on Varian A60 D, T60 and XL 100 spectrometers. ¹³C NMR spectra were measured with a Varian CFT-20 or Bruker WP-80 spectrometer. The assignment of the ¹³C NMR spectra was carried out with the help of off-resonance ¹H-decoupled ¹³C NMR spectra.

Preparation of N-methylthio-N'-(2,6-dimethylphenyl)-2,6-dimethyl-1,4-quinone-diimine (MTQD)

The procedure is a modification of that described in ref. 5, and gives a better yield of MTQD.

A solution of 3 g t-BuOH (40 mmol) in 10 cm³ of pentane was added to a solution of 3.42 g $[\text{Me}_2\text{Al}\{\text{RNS}(\text{Me})\text{NR}\}]_2$ (5 mmol) in 50 cm³ of pentane at 0° C. After the evolution of methane had ceased the mixture was stirred for 4 h at room temperature. Subsequently 5 cm³ of water was added dropwise with vigorous stirring to the dark-red solution. After 10 min the suspension was filtered off and the precipitate was washed with 3 × 25 cm³ of pentane. The solvent was removed from the filtrate under vacuum and the residual oil was dissolved in 25 cm³ of acetone. After addition of 4 cm³ of water the solution was stored at -20°C and 24 h later 1.7 g of dark red crystalline MTQD were filtered off. The crystals were washed with water and dried under vacuum for 24 h. Work-up of the filtrate yielded 0.2 g of MTQD, 0.5 g of 2,6-Me₂C₆H₃NH₂, and a sticky dark red-brown residue. Yield of MTQD 1.9 g (67%), and that of 2,6-Me₂C₆H₃NH₂ 0.5 g (21%); *m/z* for MTQD 284.134235 (C₁₇H₂₀N₂S). Crystals, suitable for X-ray determination, were obtained by sublimation (100°C/1 mmHg).

TABLE 1
CRYSTALLOGRAPHIC DATA

Formula	C ₁₇ H ₂₀ N ₂ S
Mol. weight	284
Crystal system	monoclinic
Space group	P2 ₁ /c
a	8.0471(6) Å
b	18.4471(8) Å
c	22.0383(13) Å
β	99.018(7)°
Z	4
Radiation	Cu-K _α (λ = 1.5418 Å)
Reflections	5503
R	0.069
R _w	0.071

When the same procedure was followed for [Me₂Al{RNS(Me)NR}]₂ with R = 4-MeC₆H₄ or 4-ClC₆H₄, diazoaryls (RN=NR) (25%), anilines (RNH₂) (5–10%) and polymeric products were isolated [5].

Reaction of [Me₂Al{RNS(Me)NR}]₂ (R = 2,6-Me₂C₆H₃) with 2 equivalents of t-BuOH/Al yielded, after the evolution of methane had terminated, a solution which remained colourless even when stored for 24 h at room temperature. Attempts to isolate the intermediate for the reaction leading to MTQD failed because of its high solubility in organic solvents and its extreme air- and moisture-sensitivity. Hydrolysis of the reaction mixture yielded some MTQD (>3%), 2,6-Me₂C₆H₃NH₂ (30%), and polymeric products.

X-ray crystal structure determination of MTQD

Solution and refinement. A total of 5503 independent reflections was collected with a Nonius CAD-4 single crystal diffractometer. The data were processed with the direct methods programme SIMPEL [23]. In the resulting E-map all atoms except hydrogen atoms were found. After three cycles of block-diagonal least-squares refinement it became obvious that two distinct molecules (A and B) were present in the unit cell. In each of the molecules the sulfur atom exhibited positional disorder. Three refinement cycles with isotropic temperature factors were performed in which population parameters were introduced for the sulfur atoms. This resulted in occupancies of 62 and 38% for the two sulfur positions of molecule A, and 95 and 5% for molecule B. During subsequent least-squares refinement the population parameters for the sulfur atoms were kept constant. A final R value of 0.069 was obtained for refinement in which a dispersion correction was introduced for the sulfur atoms. ($R_w = 0.071$ with a weighting scheme $w = 1.0/[2F_{\min} + F_{\text{obs}} + (2/F_{\max})F_{\text{obs}}]$.) In the final difference Fourier map the electron density nowhere exceeded a value of 0.2 e/Å³. All relevant crystallographic data are collected in Table 1. Tables of structure factors can be obtained from the authors.

Results

Molecular geometry of N-methylthio-N'-(2,6-dimethylphenyl)-2,6-dimethyl-1,4-quinonediimine (MTQD)

The X-ray structure determination of MTQD revealed the presence of two

distinct molecules (A and B, Fig. 1) in the unit cell, differing slightly in bond lengths and angles. The positions of the S-atom in molecules A and B are disordered to different extents (Fig. 1). Least square refinement showed S(1) (in molecule A) to lie with 95% probability in the position indicated with a solid line. The other possible position with 5% probability, is drawn with a broken line. The corresponding probabilities for S(2) in molecule B are 62% (solid line) and 38% (broken line), respectively. The bond lengths and angles, given in Table 2, are those derived for molecule A (Fig. 1). Fractional coordinates for both molecules A and B are given in Table 3. The C—S distance of 1.765 Å lies within the range of single bond C—S distances (1.75–1.83 Å) reported for other molecules containing an =N—S—C unit [15–17]. The N—S distance (1.649 Å) is short, but this has also been observed by Atkinson et al. in a phenylthioimine compound derived from 2,4-xyleneol (1.641 Å) [16]. The small C—S—N bond angle (98.7°) is also not unusual for a thioimine [15–17]. Noteworthy are the S—N—C (126.7°) and the N(1)—C(2)—C(7) (129.6°) angles which, in contrast to the C(5)—N(2)—C(10) (120.5°) angle, deviate strongly from the for sp^2 -N expected ideal angle of 120°. The bond lengths in the quinone-diimine fragment of the molecule clearly reflect the quinoid structure, while the other bond lengths and angles show no unusual characteristics. The atoms of the quinonediiimine unit as well as S(1), C(1) and C(10) all lie approximately

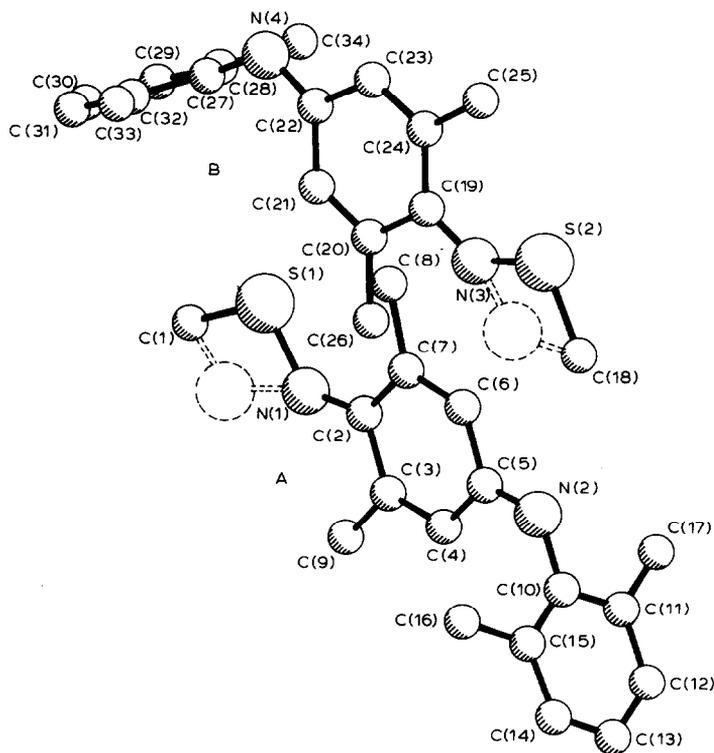


Fig. 1. The two MTQD molecules in the unit cell differ not only in bond lengths and angles but also in the degree of disorder of the S-atoms.

TABLE 2

BOND LENGTHS (Å) AND ANGLES (°). STANDARD DEVIATIONS IN PARENTHESES; THE NUMBERING OF THE ATOMS IS SHOWN IN FIGS. 1 AND 2

C(1)—S(1)	1.765(5)	C(1)—S(1)—N(1)	98.7(2)	I—II ^a	88.7(°)
C(1)—S(11)	1.619(5)	C(1)—S(11)—N(1)	127.4(3)		
S(1)—N(1)	1.649(3)	S(1)—N(1)—C(2)	126.7(3)	Δ [N(2)—I] ^b	0.156
S(11)—N(1)	1.265(3)	S(11)—N(1)—C(2)	160.7(3)	Δ [N(1)—II]	0.031
N(1)—C(2)	1.312(5)	N(1)—C(2)—C(7)	129.6(3)	Δ [N(2)—II]	0.049
C(2)—C(3)	1.481(5)	N(1)—C(2)—C(3)	113.3(3)	Δ [S(1)—II]	0.078
C(3)—C(4)	1.343(5)	C(3)—C(2)—C(7)	117.1(3)	Δ [C(1)—II]	0.196
C(3)—C(9)	1.507(5)	C(2)—C(3)—C(4)	121.4(3)	Δ [C(10)—II]	0.085
C(4)—C(5)	1.453(4)	C(2)—C(3)—C(9)	118.1(3)	Δ [C(13)—II]	0.243
C(5)—C(6)	1.440(5)	C(4)—C(3)—C(9)	120.4(3)		
C(6)—C(7)	1.353(5)	C(3)—C(4)—C(5)	121.4(3)		
C(7)—C(8)	1.512(6)	C(4)—C(5)—C(6)	117.1(3)		
C(7)—C(2)	1.470(5)	C(4)—C(5)—N(2)	124.8(3)		
C(5)—N(2)	1.303(5)	C(6)—C(5)—N(2)	118.2(3)		
N(2)—C(10)	1.420(4)	C(5)—C(6)—C(7)	123.6(3)		
C(10)—C(11)	1.383(5)	C(2)—C(7)—C(6)	119.4(3)		
C(11)—C(12)	1.395(6)	C(6)—C(7)—C(8)	118.9(3)		
C(11)—C(17)	1.487(7)	C(2)—C(7)—C(8)	121.7(3)		
C(12)—C(13)	1.382(8)	C(5)—N(2)—C(10)	120.5(3)		
C(13)—C(14)	1.359(8)	N(2)—C(10)—C(11)	120.7(3)		
C(14)—C(15)	1.389(6)	N(2)—C(10)—C(15)	117.5(3)		
C(15)—C(16)	1.497(7)	C(11)—C(10)—C(15)	121.3(3)		
C(15)—C(10)	1.404(5)	C(10)—C(11)—C(12)	118.1(4)		
S(1)—C(8)	3.017(6)	C(10)—C(11)—C(17)	121.8(4)		
		C(12)—C(11)—C(17)	120.1(4)		
		C(11)—C(12)—C(13)	121.5(5)		
		C(12)—C(13)—C(14)	119.1(4)		
		C(13)—C(14)—C(15)	122.1(4)		
		C(10)—C(15)—C(14)	117.8(4)		
		C(10)—C(15)—C(16)	121.4(4)		
		C(14)—C(15)—C(16)	120.8(4)		

^a Least squares planes defined by C(10)—C(15) (I) and C(2)—C(7) (II). ^b Deviations from I or II.

TABLE 3

POSITIONAL PARAMETERS OF THE ATOMS IN FRACTIONAL COORDINATES

Atom	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$	Atom	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$
S(1)	0.5602(1)	0.49575(6)	0.17393(6)	C(14)	0.2055(6)	0.0026(2)	0.1205(2)
S(2)	1.0386(2)	0.33322(9)	0.17474(9)	C(15)	0.2776(5)	0.0593(2)	0.1570(2)
S(11)	0.4380(0)	0.4780(0)	0.1030(0)	C(16)	0.1833(6)	0.0958(3)	0.2019(2)
S(22)	0.9013(4)	0.3430(2)	0.0975(2)	C(17)	0.6995(6)	0.0708(3)	0.1005(2)
N(1)	0.4912(4)	0.4230(2)	0.1344(2)	C(18)	0.9517(7)	0.2632(3)	0.1309(3)
N(2)	0.5203(4)	0.1340(2)	0.1919(1)	C(19)	0.0052(4)	0.4723(2)	0.1423(1)
N(3)	0.9822(4)	0.4026(2)	0.1359(2)	C(20)	0.9217(4)	0.5192(2)	0.0925(1)
N(4)	1.0715(4)	0.6957(2)	0.1546(1)	C(21)	0.9420(5)	0.5918(2)	0.0968(1)
C(1)	0.4750(7)	0.5624(2)	0.1205(3)	C(22)	1.0467(4)	0.6263(2)	0.1484(2)
C(2)	0.5091(4)	0.3554(2)	0.1530(2)	C(23)	1.1278(4)	0.5792(2)	0.1963(2)
C(3)	0.4305(5)	0.3025(2)	0.1066(2)	C(24)	1.1099(4)	0.5065(2)	0.1952(2)
C(4)	0.4326(4)	0.2311(2)	0.1185(1)	C(25)	1.1935(5)	0.4606(2)	0.2473(2)
C(5)	0.5157(4)	0.2023(2)	0.1768(1)	C(26)	0.8139(6)	0.4855(2)	0.0374(2)
C(6)	0.5970(5)	0.2536(2)	0.2209(2)	C(27)	0.9902(5)	0.7457(2)	0.1104(2)
C(7)	0.5952(4)	0.3261(2)	0.2116(2)	C(28)	1.0720(6)	0.7693(2)	0.0631(2)
C(8)	0.6830(8)	0.3748(3)	0.2618(2)	C(29)	0.9952(6)	0.8227(2)	0.0231(2)
C(9)	0.3430(6)	0.3312(2)	0.0459(2)	C(30)	0.8431(7)	0.8531(2)	0.0315(2)
C(10)	0.4408(4)	0.0811(2)	0.1503(1)	C(31)	0.7639(7)	0.8301(3)	0.0796(2)
C(11)	0.5289(5)	0.0466(2)	0.1095(2)	C(32)	0.8357(6)	0.7765(2)	0.1199(2)
C(12)	0.4506(7)	-0.0107(2)	0.0749(2)	C(33)	0.7485(8)	0.7520(3)	0.1720(3)
C(13)	0.2901(7)	-0.0331(3)	0.0809(2)	C(34)	1.2376(7)	0.7382(4)	0.0546(3)

in one plane (Table 2 and Fig. 2), C(1) having the largest deviation (0.2 Å). The atoms C(10)–C(17) of the *ortho*-xylyl fragment of the molecule also lie in one plane. In contrast N(2) slightly deviates from this latter plane (0.15 Å). Finally we note that both mentioned planes are almost perpendicular to each other (Table 2 and Fig. 2).

Temperature dependence of the ^1H NMR spectrum of MTQD

The ^1H NMR spectrum of MTQD at high temperatures ($>40^\circ\text{C}$) could easily be explained on basis of the molecular geometry found for this molecule in the solid (Table 4 and Fig. 3). The Me(2') and H(3'), H(4') of the xylyl ring could readily be assigned by comparison of the ^1H NMR results with those derived for $\text{RN}=\text{S}=\text{NR}$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) [5]. The assignment of the *S*-Me group was made by comparison with $\text{RNHS}(\text{Me})\text{O}$ [5] and $(4\text{-MeC}_6\text{H}_4)_2\text{C}=\text{NSMe}$ [25]. Since the resonances of the hydrogen atom at the 3-position and of the methyl group at the 2-position are expected to be shifted upfield under influence of the π system of the *o*-xylyl group (0.80 and 0.28 ppm theoretically) they were assigned to the furthest upfield multiplet at 5.95 and doublet at 2.08 ppm, respectively. The remaining multiplet at 6.70 and doublet at 2.33

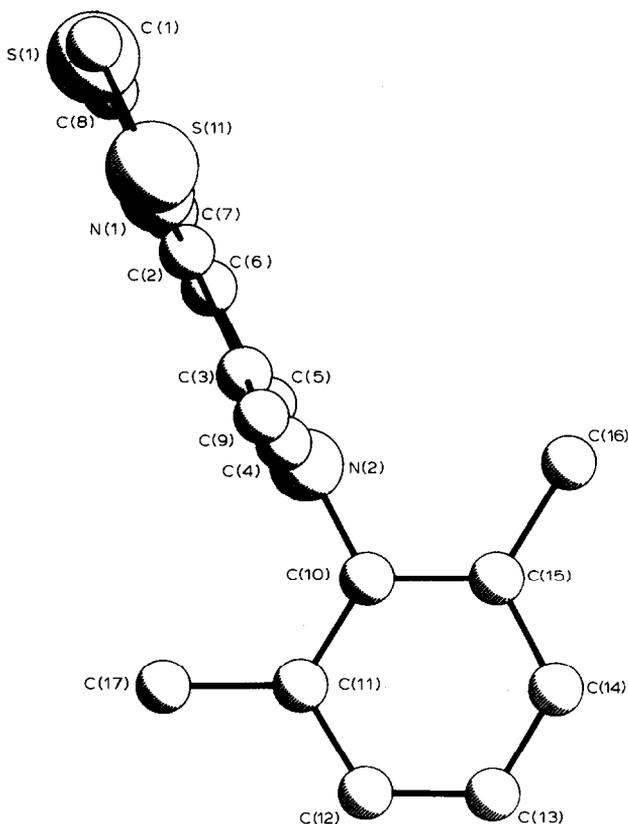


Fig. 2. The MTQD molecule seen from a point of view almost perpendicular on the xylyl ring. The quinonediimine ring and the N–S–Me unit lie in one plane.

TABLE 4
 ^1H AND ^{13}C NMR DATA FOR MTQD IN CDCl_3 VALUES IN PPM RELATIVE TO TMS. THE NUMBERING OF THE ATOMS IS GIVEN IN FIG. 3

Temperature ($^{\circ}\text{C}$)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(1')	C(2')	C(3')	C(4')	S-Me	Me(2)	Me(6)	Me(2')	Me(6')
^1H :															
+67	--	--	5.95	--	6.70	--	--	--	6.80-7.10	6.80-7.10	2.80	2.08	2.33	1.95	
	--	--	5.93	--	6.72	--	--	--	6.80-7.10	6.80-7.10	2.83	2.13	2.52	1.97	
-63	--	--	5.92 ^a	--	6.72 ^a	--	--	--	6.80-7.10	6.80-7.10	2.83	1.95	2.30	1.97	
^{13}C :															
+65	158.85	139.68	119.39	153.80	131.18	141.29	149.00	126.15	127.55	122.88	27.67	20.55	20.77	17.86	
	158.73	142.48	121.03	152.92	132.40	143.56	148.23	126.03	127.19	122.56	27.53	22.78	22.80	18.14	
-65	158.53	136.44	116.58	152.83	127.49	138.43	148.23	136.03	127.19	122.56	27.44	19.29	19.43	18.14	
Δ ^b	0.2	5.04	4.45	0.09	4.91	5.13	0	0	0	0	0.09	3.49	3.37	0	

^a $J(\text{Me}(2)-\text{H}(3)) = J(\text{Me}(6)-\text{H}(5)) = 1.5$ Hz and $J(\text{H}(3)-\text{H}(5)) = 2$ Hz. ^b Chemical shift difference between both isomers.

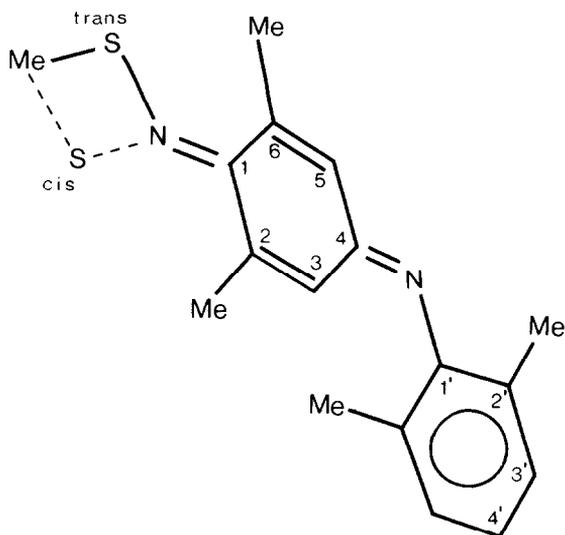


Fig. 3. *Cis*- and *trans*-conformers of MTQD. Both conformers are present in solution as well as in the solid state. Numbering of the atoms used in the discussion of the NMR data.

ppm were assigned to the H(5) and Me(6) groups of the quinonediimine ring. The latter assignments were supported by the results of homonuclear decoupling experiments: saturation of the Me(2) spin system resulted in transformation of the H(3) multiplet into a doublet with a coupling constant of 2 Hz. Likewise, saturation of the Me(6) led to a doublet for the H(5) signal with the same coupling constant. This coupling constant was assigned to $J(\text{H}(3)\text{--H}(5))$. When the temperature is lowered, the H(3) and H(5) multiplets broaden somewhat. In contrast, the Me(2) and Me(6) resonances change much more drastically: both resonances broaden, until at approximately -20°C , four doublets instead of two are present, and these become sharper upon further cooling. This indicates the presence of two conformers in solution which are in equilibrium with each other.

Temperature dependence of the ^{13}C NMR spectrum of MTQD

The S-Me, Me(2'), and 1'- to 4'- ^{13}C resonances in the spectrum obtained at $+65^\circ\text{C}$, were assigned by comparison with ^{13}C results derived for RNHS(Me)O (R = 2,6-Me₂C₆H₃); [5] (Table 4 and Fig. 3). Assignment of the C(2), C(3), C(5) and C(6) atoms is based on comparison with compounds which contain a similar *cis*-HC=CCH₃ unit. Again the resonances of the atoms at the 2- and 3-positions are shifted upfield with respect to those of the atoms at the 6- and 5-positions under the influence of the xylyl group. The two remaining resonances are assigned to the 1- and 4-carbon atoms. Which one of the two carbon atoms belongs to the most down-field resonance remains doubtful, although the low temperature spectra of the compound strongly suggest it to be C(1) (*vide infra*). Lowering of the temperature causes all the signals except those of the xylyl group to broaden, and at very low temperature ($<60^\circ\text{C}$) these signals are all doubled (Table 4 and Fig. 4). The separation of the two resonances

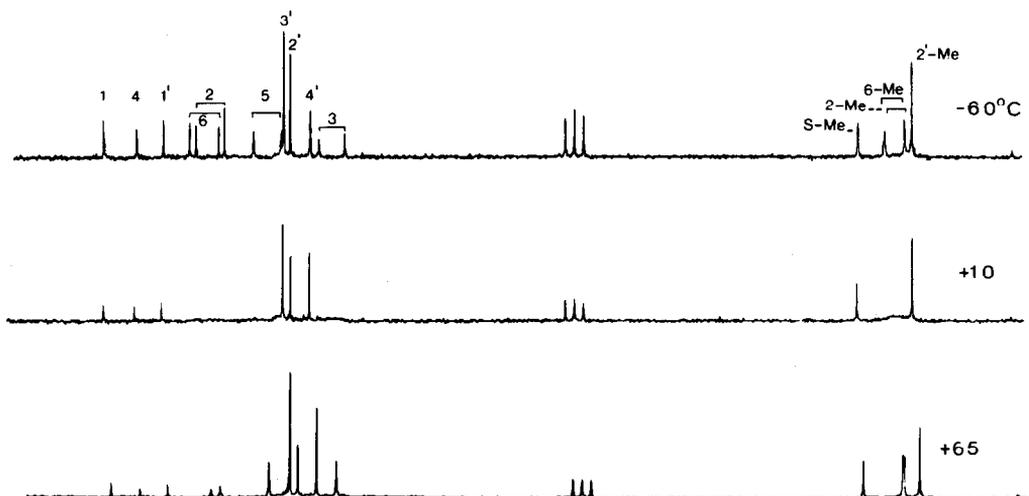


Fig. 4. Temperature dependence of the ^{13}C NMR spectrum of MTQD. The numbering of the resonances corresponds with Fig. 3.

belonging to C(1) (0.2 ppm) is twice as large as that of the C(4) resonances (0.09 ppm). On the other hand, the separation of both C(3) resonances deviates by only 10% from that found for both C(5) signals. The same observation can be made for the C(2) and C(6), and Me(2) and Me(6) ^{13}C resonances (Table 4). The coalescence point of both Me(2) resonances could be determined with sufficient accuracy ($10^\circ\text{C} \pm 1$) to make an estimate of the free energy of activation ΔG^\ddagger . Use of the well-known expression for the rate constant at coalescence $k_c = \pi\Delta\nu/V_2$ in conjunction with the Eyring equation [24] gives $\Delta G^\ddagger = 13.7 \pm 1.0$ kcal/mol for the dynamic process which is clearly occurring in solution.

Discussion

It has been shown previously that transition metal complexes containing $[\text{RNS}(\text{R}')\text{NR}]^-$ ligands decompose quantitatively in solution into $\text{RN}=\text{NR}$ and SR' fragments [7,12,14]. It was concluded that for all these metal complexes the formation of $\text{RN}=\text{NR}$ proceeds intramolecularly via intermediates, which are likely monomeric in nature. The decomposition of aluminium compounds of this type proved to be much less specific: in addition to $\text{RN}=\text{NR}$, RNH_2 and polymeric materials were also isolated, indicating that in this case intermolecular reactions also play a role in the decomposition [5]. Hydrolysis of $[\text{Me}_2\text{Al}\{\text{RNS}(\text{Me})\text{NR}\}]_2$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) with $t\text{-BuOH}$ yielding N -methylthio- N' -(2,6-dimethylphenyl)-2,6-dimethyl-1,4-quinonediimine (MTQD) represents an exception to the general observation that hydrolysis of complexes of this type gives $\text{RN}=\text{NR}$ and RNH_2 [5,7].

Structure of MTQD in the solid state

The bond lengths in the quinonediimine unit of the molecule (Table 2 and

Fig. 1) strongly reflect its quinoid character: thus the C(6)—C(7) and C(2)—C(3) distances are shortened while the other bond lengths are lengthened. The N(1)—C(2) and N(2)—C(5) distances are typical of a C—N double bond [16,20]. The N(2)—C(10) distance of 1.42 Å is not unusual for a N—Ph single bond, and may be compared with C—N distances reported for various anilines [18,19]. The *o*-xylyl fragment of the molecule also contains no anomalies. The angle between the quinonediimine, and the *o*-xylyl ring in the molecule leads to minimal sterical hindrance between the *o*-methyl groups of the xylyl ring and the hydrogen atom attached to C(4). Some unusual features of the molecule are found in the =NSMe unit: while the C(1)—S(1) distance is as expected for a single bond, the S(1)—N(1) distance is unusually short. In view of this result it is informative to recall that the N—S distance in (CO)₂Rh{RNS(R')-NR}, where the N—S bond formally has a bond order of 1.5, is also 1.65 Å [12]. This short N(1)—S(1) distance could be explained by conjugation, which would mean involvement of *S-d* orbitals in the bonding. However, if the N—S bond is involved with the quinonediimine unit in a conjugated system, we would expect the N(1)—C(2) distance to be lengthened, which it is not. This demonstrates that great care must be exercised in relating the bond-order of a N—S bond to the bond length, especially since Roesky et al. [26] found the bond length to be related to the coordination number of the S atom rather than to the bond order of the N—S bond. The planarity of the N—S—Me unit, which lies in the plane of the quinonediimine fragment (Table 2 and Fig. 2), may be explained by the short distance between S(1) and the C(8) methyl group (S(1)—C(8) = 3.00 Å). Thus the orientation of the S-atom gives minimal repulsive interaction between the S-lone pairs and the C(8) methyl group. Such steric interaction would also account for the unusually large S(1)—N(1)—C(2) (126.7°) and N(1)—C(2)—C(7) (129.6°) bond angles. The disordering of the sulfur atoms means that there are two conformational isomers of the molecule present in the unit cell; in one conformer the xylyl ring and the S-atom are *trans*-oriented with respect to each other, (78.5% abundant) and in the other they have a *cis*-orientation with the *S*-Me group still in the same position.

Dynamical behaviour of MTQD in solution

In the solid state 22.5% of the molecules have a *cis*- and the others a *trans*-conformation. However, when they are dissolved this distribution is changed rapidly as can be seen from NMR measurements. This strongly suggests that the dynamic process which occurs in solution is *cis*—*trans* exchange. This exchange could be accomplished in several ways:

(1) Flipping of the xylyl group by rotation around the N=C double bond or by inversion of the N-atom. This would inter alia mean exchange of the 5(*trans*) and 3(*cis*) as well as the 3(*trans*) and 5(*cis*) carbon atoms. However, the ¹³C spectra of MTQD show that the 5(*trans*) carbon atom exchanges with the 5(*cis*) atom and the 3(*trans*) with the 3(*cis*). On these grounds xylyl-flipping can be excluded.

(2) Flipping of the S-atom by rotation around the N=C double bond, inversion of the N-atom followed by rotation around the N—S bond, or inversion of the sulfur atom.

These latter processes are all consistent with the observed temperature depen-

dent behaviour of the NMR spectra of MTQD. The derived free energy of activation ΔG^\ddagger (13.7 kcal/mol) is small compared with that for the *cis*–*trans* isomerization of $(4\text{-MeC}_6\text{H}_4)_2\text{C}=\text{NSMe}$ (18.5 kcal/mol) [25]. Since it has been shown that the presence of a strongly conjugating group on the N-atom decreases both the barrier for rotation around the N=C bond and the barrier for N-inversion [25], no definite conclusion can be drawn about the nature of the *cis*–*trans* isomerization. However, since the solid-state molecular geometry indicates the presence of a (repulsive) steric interaction between the methyl group on the quinonediimine ring and the S lone pairs, an N inversion mechanism seems more likely, especially since such steric hindrance is expected to cause a decrease in ΔG^\ddagger for the inversion mechanism [25].

Formation of MTQD

Reaction of $[\text{Me}_2\text{Al}\{\text{RNS}(\text{Me})\text{NR}\}]_2$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) with 2 molar equivalents of *t*-BuOH results in a rapid evolution of methane, the reaction mixture remaining colourless. After addition of another equivalent of *t*-BuOH the reaction mixture slowly becomes dark-red, indicating that MTQD is formed. It is impossible to decide the details of the reaction leading to MTQD on basis of the available data, some suggestions about the general outlines of the reaction scheme, can be offered.

The first step in the reaction is likely to be replacement of all the methyl groups on Al by *t*-BuO groups. In view of results derived for similar compounds [5], the resulting species (I Fig. 5) is most probably still a dimer. Reaction of such a dimer with another equivalent of *t*-BuOH would produce a monomeric

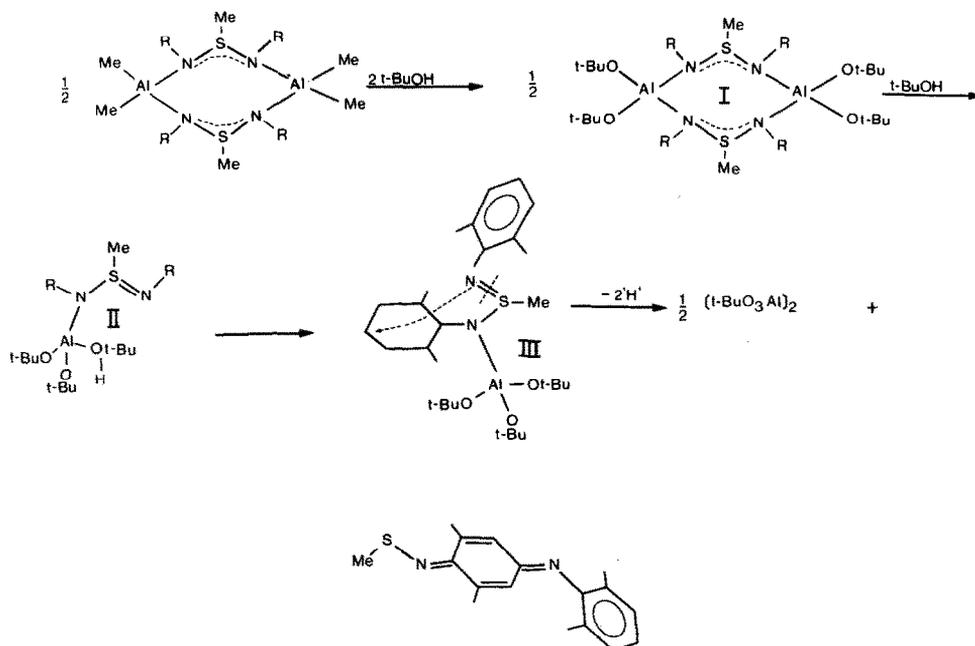


Fig. 5. Reaction scheme for the formation of MTQD.

species in which the sulfurdiimine ligand is monodentate (II Fig. 5). Monodentate-bonded $[RNS(R')NR]$ has been shown to be unstable [5,7] and is reported to decompose with formation of $RN=NR$. However, the structure of MTQD suggests that in this particular case only one of the N—S bonds is cleaved. Moreover, the high yield suggests that an intramolecular mechanism operates. We therefore propose an intermediate (III Fig. 5) in which one of the nitrogen atoms is positioned above the plane of the *o*-xylyl ring. Study of models shows that the formation of such an intermediate would be favoured by the fact that it has a conformation with minimal sterical hindrance. The subsequent steps in the reaction scheme involve N—S bond cleavage, migration of the $[2,6-Me_2C_6H_3N]$ unit, and abstraction of two hydrogen atoms.

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