

CCA-1932

YU ISSN 0011-1643

UDC 547.787

Note

Description of Molecular Distortions: IV. Relationships Between the Distortion and the Hydrogen Bond Strength for Some Compounds Containing HSO_4 Ions

V. Petruševski

*Institute of Chemistry, Faculty of Science,
Skopje, Yugoslavia*

and

A. W. Al-Kassab, B. D. James and J. Liesegang

Department of Chemistry, La Trobe University, Bundoora, Victoria, 3038, Australia

Received June 21, 1989

Several methods are known for describing the distortions of tetrahedral molecules. In the present paper, some correlations between the hydrogen bond strength and the different measures for the distortions of HSO_4^- ions are evaluated. In terms of the distortion indices the results reflect similar trends to those calculated for phosphates¹. It is found that weaker hydrogen bonding is accompanied by larger distortions of the HSO_4 tetrahedra.

INTRODUCTION

Previous works have shown that hydrogen bonding has a remarkable role in modifying the oxo-anions geometry in the HXO_4 and H_2XO_4 groups to which the hydrogen atom is attached¹⁻³. Thus, the existence of correlations between the three distortion indices⁴ and the hydrogen bond length¹ for some hydrogenphosphates, as well as correlations between X-O(H) and O-H...O distances (in which X = B, C, N, S, Si, As, Se, I)^{2,3} for a number of hydrogen tetraoxoanions, were revealed. The distortions of polyatomic molecules (or ions) in the solid state, however, may be described in a variety of ways⁴⁻¹⁰ each method having some advantages and some shortcomings. It is therefore of interest to study the effect of hydrogen bonding in some hydrogensulfates, especially on the distortion indices⁴, displacement vectors⁶ and the total distortion⁹ of these ions.

DEFINITIONS AND CALCULATIONS

All quantities were defined in the original papers^{4,6,9}.

A total of 39 hydrogensulfate ions from 30 different crystal structures^[11-40] have been investigated. Data for $\text{Ba}(\text{HSO}_4)_2$ were not included in the regression analysis because the hydrogen bonds in this compound are exceptionally weak (Table I). Inaccurate structures (estimated standard deviation of bond-lengths > 1 pm) were also excluded. Compounds with proton-disorder were

TABLE I
Distortions and hydrogen bond strengths for some hydrogensulfates (data marked
with* were not included in the regression analysis)

Compound	DI(TO)	DI(CTO)	DI(OC)	$ D_2 /^\circ$	$ D_3 /\text{pm}$	$ D_4 /^\circ$	Dt	R(O...O)/pm	Ref.
KHSO ₄ '	0.0292	0.0310	0.0056	1.74	10.90	8.16	0.06410	261.9	[11]
KHSO ₄ '	0.0265	0.0348	0.0066	2.46	10.17	8.32	0.05973	263.0	[12]
KHSO ₄ '	0.0313	0.0304	0.0039	1.57	10.16	9.92	0.06378	257.3	[11]
KHSO ₄ '	0.0298	0.0354	0.0065	1.74	10.51	10.20	0.06756	258.3	[12]
C ₆ H ₅ N ₃ HSO ₄	0.0256	0.0309	0.0064	1.99	8.77	8.57	0.05019	256.5	[13]
C ₁₂ H ₁₈ N ₆ H ₂ SO ₄	0.0313	0.0314	0.0074	2.90	10.69	8.87	0.06407	259.4	[14]
[Co ₂ (NH ₃) ₁₀ O ₂](HSO ₄) ₃ SO ₄	0.0311	0.0284	0.0058	2.20	10.82	7.81	0.06161	255.0	[15]
[Co ₂ (NH ₃) ₁₀ O ₂](HSO ₄) ₃ SO ₄	0.0328	0.0338	0.0046	1.68	11.57	9.69	0.07350	260.0	[15]
Rb ₃ H(SO ₄) ₂	0.0199	0.0250	0.0035	0.28	6.86	6.72	0.03268	248.5	[16]
Pt(NH ₃) ₄ PtBr ₂ (NH ₃) ₄ (HSO ₄) ₄	0.0287	0.0277	0.0075	3.34	10.15	8.07	0.05951	258.2	[17]
NaHSO ₄ ·H ₂ O	0.0409	0.0318	0.0121	4.09	14.54	9.81	0.09529	270.0	[18]
NaHSO ₄ ·H ₂ O	0.0372	0.0266	0.0123	4.21	12.85	7.37	0.07420	265.8	[19]
Na ₃ H(SO ₄) ₂	0.0160	0.0158	0.0041	1.78	5.62	4.35	0.02103	243.2	[20]
Na ₂ H(SO ₄) ₂	0.0168	0.0155	0.0041	1.44	5.91	4.35	0.02240	243.4	[21]
H ₂ SO ₄	0.0374	0.0355	0.0123	5.52	11.06	10.28	0.07481	263.0	[22]
CH ₃ C(OH) ₂ HSO ₄	0.0261	0.0313	0.0036	0.52	8.83	8.44	0.05098	256.7	[23]
NaHSO ₄ '-α	0.0158	0.0125	0.0045	1.87	4.81	3.98	0.01695	249.7	[24]
NaHSO ₄ '-α	0.0355	0.0329	0.0073	2.73	12.24	8.94	0.07607	269.0	[24]
CsHSO ₄	0.0251	0.0217	0.0083	2.91	7.53	7.81	0.04008	257.2	[25]
(ND ₁) ₂ D(SO ₄) ₂	0.0179	0.0185	0.0001	0.27	6.09	4.97	0.02454	255.9	[26]
(ND ₄) ₃ D(SO ₄) ₂ -III	0.0216	0.0217	0.0033	1.40	7.84	6.02	0.03848	254.4	[27]
(ND ₄) ₃ D(SO ₄) ₂ '-III	0.0191	0.0255	0.0050	1.34	7.05	7.09	0.03527	253.6	[27]
(NH ₄) ₃ H(SO ₄) ₂	0.0179	0.0183	0.0012	0.12	6.10	4.94	0.02444	254.1	[28]
(NH ₄) ₃ H(SO ₄) ₂	0.0170	0.0180	0.0015	0.83	5.77	4.84	0.02269	254.0	[29]
[C ₂ H ₂₅ N ₅ O]HSO ₄ ·(1/2)H ₂ O	0.0219	0.0312	0.0093	0.80	6.57	3.99	0.02538	261.4	[30]
[Ag(C ³ H ₇ N ₁₀)]SO ₄ HSO ₄ ·H ₂ O	0.0283	0.0312	0.0061	2.59	9.76	8.35	0.05704	251.0	[31]
H ₂ SO ₄ ·H ₂ O	0.0284	0.0258	0.0086	3.08	9.87	7.61	0.05471	265.7	[32]
NH ₄ HSO ₄ '	0.0298	0.0344	0.0125	5.28	10.16	10.05	0.06548	251.4	[33]
NH ₄ HSO ₄ '	0.0286	0.0306	0.0054	1.78	9.81	8.63	0.05709	259.8	[34]
[CoCl ₂ (NH ₃) ₄ HSO ₄	0.0329	0.0325	0.0067	2.84	11.19	8.75	0.06794	261.7	[35]
C ₁₅ H ₁₈ ClN ₄ O ₃ SHSO ₄	0.0235	0.0292	0.0282	2.10	8.54	8.71	0.04880	265.9	[36]
Mg(HSO ₄) ₂	0.0273	0.0266	0.0076	2.26	9.34	7.87	0.05069	276.8	[37]
Ca(HSO ₄) ₂ '	0.0224	0.0271	0.0122	3.84	8.06	8.30	0.04304	262.0	[38]
Ca(HSO ₄) ₂ '	0.0300	0.0336	0.0081	3.71	10.65	9.31	0.06690	252.2	[38]
RbHSO ₄ '	0.0304	0.0305	0.0117	4.80	10.08	10.09	0.06669	253.0	[39]
RbHSO ₄ '	0.0361	0.0381	0.0057	2.27	12.49	10.31	0.08360	262.0	[39]
Ba(HSO ₄) ₂ '*	0.0297	0.0260	0.0099	1.66	10.31	7.41	0.05629	283.0	[40]
Ba(HSO ₄) ₂ '**	0.0309	0.0339	0.0121	4.82	10.52	9.49	0.06972	281.6	[40]

also excluded, unless the proton was disordered between the proton-donor and the proton-acceptor. H_2SO_4 was considered as the only known example of a dihydrogensulfate compound.

Calculations of the distortion indices $\text{DI}(\text{TO})$, $\text{DI}(\text{OTO})$ and $\text{DI}(\text{OO})$, displacement vectors ($\mathbf{D}_2(\text{E})$, $\mathbf{D}_3(\text{F}_2)$ and $\mathbf{D}_4(\text{F}_2)$), the total distortion (D_t) and the regression analyses were performed on a Commodore 128 micro-computer with a suitable programs written in Basic. The input data were the unit-cell parameters and the fractional coordinates of the five atoms (S, O₁, O₂, O₃, O₄). The bondlengths were not corrected for thermal motion.

RESULTS AND DISCUSSION

The distortions and the hydrogen-bond strengths for the investigated compounds are presented in Table I, and the least-squares-best-fit lines are given in Table II. Somewhat surprisingly, the r value for the correlation between $\text{DI}(\text{OTO})$ and $R(\text{O} \dots \text{O})$ is somewhat lower than the r value for the $\text{DI}(\text{OO})$ - $R(\text{O} \dots \text{O})$ correlation. It is expected that $\text{DI}(\text{OO})$ should be the most »independent« distortion index, since it has been shown that the distortion of tetrahedral oxo-anions may be visualized as »a central atom moving in a rigid framework of oxygens«^{4,41} With respect to this, the results for hydrogen-sulfates clearly differ from those obtained for hydrogenphosphates¹.

TABLE II

Regression relationships for the distortion indices referred to in the text

Hydrogen Sulfate Distortion Indices	Least-squares-best-fit Regression Formula	r
$\text{DI}(\text{TO})$	$6.02 \times 10^{-4} \times R(\text{O} \dots \text{O})/\text{pm} - 0.1285$	0.63
$\text{DI}(\text{OTO})$	$4.22 \times 10^{-4} \times R(\text{O} \dots \text{O})/\text{pm} - 0.0816$	0.44
$\text{DI}(\text{OO})$	$2.20 \times 10^{-4} \times R(\text{O} \dots \text{O})/\text{pm} - 0.0502$	0.46
$ \mathbf{D}_2(\text{E}) /^\circ$	$0.0655 \times R(\text{O} \dots \text{O})/\text{pm} - 14.64$	0.33
$ \mathbf{D}_3(\text{F}_2) /\text{pm}$	$0.209 \times R(\text{O} \dots \text{O})/\text{pm} - 44.79$	0.63
$ \mathbf{D}_4(\text{F}_2) /^\circ$	$6.127 \times R(\text{O} \dots \text{O})/\text{pm} - 25.00$	0.46
D_t	$1.67 \times 10^{-3} \times R(\text{O} \dots \text{O})/\text{pm} - 0.3792$	0.59

The lowest value for r (0.33) was obtained for the regression of $|\mathbf{D}_2(\text{E})|$ on $R(\text{O} \dots \text{O})$, as expected. It has been shown by Murray-Rust *et al.*^[5] that for distortions preserving C_3 co-kernel (or effective) symmetry, $\mathbf{D}_2(\text{E}) = 0$, so the values for this distortion vector are expected to be much smaller than the values for $\mathbf{D}_4(\text{F}_2)$ and this is, indeed, the case (see Table I). Once again, the highest value for r (Table II) is obtained for the regression of $|\mathbf{D}_3(\text{F}_2)|$ on $R(\text{O} \dots \text{O})$ $\mathbf{D}_3(\text{F}_2)$ being the vector analogy of the distortion index $\text{DI}(\text{TO})$. The correlation coefficient for the regression of D_t on $R(\text{O} \dots \text{O})$ is, also, rather high.

Despite the rigorous criteria under which the structures were taken into consideration, the scatter of the points (especially in the case of $\text{DI}(\text{OTO})$, $\text{DI}(\text{OO})$, $|\mathbf{D}_2(\text{E})|/^\circ$ and $|\mathbf{D}_4(\text{F}_2)|/^\circ$ correlations) is very large (the situation with the hydrogenphosphate-correlations is quite similar). Since this scatter is not a result of inaccuracies in the crystal-structure determinations, it indicates that, although important, the hydrogen bonding is far from being the only cause for the distortions of oxo-anions in crystals. In a more sophisticated

approach, the interaction with (metal) cations must be taken into account. Moreover, the recent works of Finney and Savage^[42,43] reveal the importance of the so-called non-bonded interactions in minimizing the crystal energy. Obviously, further work is needed to estimate the effect of these interactions on the distortion of polyatomic molecules and ions in crystals.

Acknowledgement. — The financial support of the Community for Scientific Activities of SR Macedonia (V.P.) and the Australian Research Council (B.D.J., J.L.) is gratefully acknowledged.

REFERENCES

1. M. Ichikawa, *Acta Crystallogr.*, **B43**, (1987) 23.
2. G. Ferraris and G. Ivaldi, *Acta Crystallogr.*, **B40**, (1980) 1.
3. M. Catti, G. Ferraris and G. Ivaldi, *Acta Crystallogr.*, **B35**, (1979) 525.
4. W. H. Baur, *Acta Crystallogr.*, **B30**, (1974) 1195.
5. P. Murray-Rust, H. B. Bürgi and J. D. Dunitz, *Acta Crystallogr.*, **B34**, (1978) 1787.
6. P. Murray-Rust, H. B. Bürgi and J. D. Dunitz, *Acta Crystallogr.*, **B34**, (1978) 1793.
7. P. Murray-Rust, H. B. Bürgi and J. D. Dunitz, *Acta Crystallogr.*, **A35**, (1979) 703.
8. W. A. Dollase, *Acta Crystallogr.*, **A30**, (1974) 513.
9. V. Petrševski and K. Trenčevski, *Croat. Chem. Acta*, **59**, (1986) 867.
10. V. Petrushevski and B. Soptrajanov, *J. Mol. Struct.*, **175**, (1988) 349.
11. F. Payan and R. Haser, *Acta Crystallogr.*, **B32**, (1976) 1875.
12. F. A. Cotton, B. A. Frenz and D. L. Hunter, *Acta Crystallogr.*, **B31**, (1975) 302.
13. F. Giordano, *Acta Crystallogr.*, **B36**, (1980) 2458.
14. G. Thevenet and N. Rodier, *Acta Crystallogr.*, **B34**, (1978) 1280.
15. W. P. Schaefer, S. E. Ealick and R. E. Marsh, *Acta Crystallogr.*, **B37**, (1981) 34.
16. S. Fortier, M. E. Fraser and R. D. Heyding, *Acta Crystallogr.*, **C41**, (1985) 1139.
17. M. Tanaka, I. Tsujikawa, K. Toriumi and T. Ito, *Acta Crystallogr.*, **B38**, (1982) 2793.
18. G. E. Pringle and T. A. Broadbent, *Acta Crystallogr.*, **19**, (1965) 426.
19. S. Grimvall, *Acta Crystallogr.*, **25**, (1971) 3213.
20. W. Joswig, H. Fuess and G. Ferraris, *Acta Crystallogr.*, **B38**, (1982) 2798.
21. M. Catti, G. Ferraris and G. Ivaldi, *Acta Crystallogr.*, **B35**, (1979) 525.
22. C. Pascard-Billy, *Acta Crystallogr.*, **18**, (1965) 829.
23. P.-G. Jönsson and I. Olovsson, *Acta Crystallogr.*, **B24**, (1968) 559.
24. E. J. Sonneveld and J. W. Visser, *Acta Crystallogr.*, **B35** (1979) 1975.
25. K. Itoh, T. Ozaki and E. Nakamura, *Acta Crystallogr.*, **B37**, (1981) 1908.
26. M. Tanaka and Y. Shiozaki, *Acta Crystallogr.*, **B37**, (1981) 1171.
27. M. Tanaka and Y. Shiozaki, *Acta Crystallogr.*, **B37**, (1986) 776.
28. A. Leclaire, M. Ledeséert, J. C. Menier, A. Daoud et M. Damak, *Acta Crystallogr.*, **B41**, (1985) 209.
29. S. Suzuki and Y. Makita, *Acta Crystallogr.*, **B34**, (1978) 732.
30. O. I. Levina, E. N. Kurkutova and K. A. Potekhin, *Cryst. Struct. Comm.*, **11**, (1982) 1915.
31. L. Coghi and G. Pelizzi, *Acta Crystallogr.*, **B31**, (1975) 131.
32. I. Taesler and I. Olovsson, *Acta Crystallogr.* **B24**, (1968) 299. (1980) 210.
33. R. J. Nelmes, *Acta Crystallogr.*, **B27**, (1971) 272.
34. J.-A. P. Bonapace and N. S. Mandel, *Acta Crystallogr.*, **B31**, (1975) 2540.
35. L. Dupont, O. Dideberg et J. Toussaint, *Acta Crystallogr.*, **B36**, (1980) 210.
36. M. A. Simonov, S. I. Troyanov, E. Kemnitz, D. Haas and M. Kammler, *Kristallografiya*, **31**, (1986) 1220.

37. S. I. Troyanov, M. A. Simonov, E. Kemnitz, D. Hass and B. Gruntze, *Dokl. Akad. Nauk. SSSR*, **283**, (1985) 1241.
38. D. Hass, E. Kemnitz, R. Sekowski and Worzala, *Z. Anorg. Allg. Chem.*, **525**, (1985) 173.
39. J. P. Ashmore and H. E. Petch, *Can. J. Phys.*, **53**, (1975) 2694.
40. S. I. Troyanov, M. A. Simonov, E. Kemnitz, D. Hass and M. Kammler, *Dokl. Akad. Nauk. SSSR*, **288**, (1986) 1376.
41. W. H. Baur, *Trans. Am. Crystallogr. Assoc.*, **6**, (1970) 129.
42. J. L. Finney, and H. F. J. Savage *VIIIth Workshop Horizons in Hydrogen Bond Research. Abstracts 6*, Polanica Zdrój (1987).
43. H. F. J. Savage and J. L. Finney, *Nature*, **322**, (1986) 717.

SAŽETAK

Opis molekulskih distorzija: IV. Odnos između veličine distorzije i jakosti vodikove veze u spojevima s HSO_4^- ionima

V. Petruševski, A. W. Al-Kassab, B. D. James i J. Liesegang

Procijenjene su korelacije jakosti vodikove veze s nekim mjerama za distorziju iona HSO_4 . Rezultati su uspoređeni s onima za fosfate. Slabija vodikova veza obično je združena s većom distorzijom HSO_4 -tetraedra.