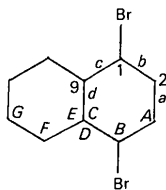


Table 2. Mean bond lengths (Å) and angles (°) in naphthalene and 1,4-dibromonaphthalene (numbers in parentheses are standard deviations of the means calculated from the LS e.s.d.'s and independently from the r.m.s. deviations from the means for the dibromo compound)



	Naphthalene		Dibromonaphthalene	
	Cruickshank (1957) (no libration correction)	Pawley & Yeats (1969)	<i>mmm</i>	<i>mm</i>
<i>a</i>	1.416 (6)	1.401 (7)	1.393 (9,14)	1.410 (12,9) 1.376 (12,23)
<i>b</i>	1.357 (4)	1.372 (5)	1.368 (6,4)	1.370 (9,7) 1.366 (9,6)
<i>c</i>	1.420 (3)	1.423 (5)	1.409 (6,6)	1.407 (8,9) 1.411 (8,9)
<i>d</i>	1.405 (6)	1.412 (7)	1.422 (11,16)	1.422 (11,16)
Br—C	—	—	1.917 (6,6)	1.917 (6,6)
<i>A</i>	120.5 (2)	120.7 (1)		118.7 (6,5)
<i>B</i>	120.3 (3)	120.2 (2)		123.8 (6,5)
<i>C</i>	119.2 (2)	119.2 (1)		117.6 (6,6)
<i>D</i>	121.5 (3)	[121.6 (1)]		123.6 (6,4)
<i>E</i>	119.2 (2)	119.2 (1)		118.8 (6,9)
<i>F</i>	120.3 (3)	120.2 (2)		120.2 (6,3)
<i>G</i>	120.5 (2)	120.7 (1)		120.9 (6,5)
Br—C(1)—C(2) type	—	—		116.5 (5,7)
Br—C(1)—C(9) type	—	—		119.7 (5,3)

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## Interatomic Distances and Angles in Four Planar Systems with Adjacent C—O and C—N Bonds: Structures of Pivalamide (I), Dipivalamide (II), *N*-Pivaloylpivalamidinium Pyrosulfate (III) and *N*-Pivaloylpivalamidine (IV)

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**Abstract.** 2,2-Dimethylpropionamide (pivalamide), C<sub>5</sub>H<sub>11</sub>NO (I): *M<sub>r</sub>* = 101.15, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 10.303 (1), *b* = 5.896 (1), *c* = 10.404 (2) Å, β = 102.65 (1)°, *V* = 616.7 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.1 (1), *D<sub>x</sub>* = 1.0894 (3) Mg m<sup>-3</sup>, Mo *Kα*, λ = 0.71069 Å for

graphite-monochromatized radiation, μ(Mo *Kα*) = 0.071 mm<sup>-1</sup>, *T* = 140 K, *F*(000) = 224, *R* = 0.044 for 1035 unique reflections. Bis(2,2-dimethylpropionyl)-amine (dipivalamide), C<sub>10</sub>H<sub>19</sub>NO<sub>2</sub> (II): *M<sub>r</sub>* = 185.27, orthorhombic, *Pcab*, *a* = 10.889 (8), *b* = 11.545 (15),

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$c = 17.769$  (28) Å,  $V = 2234$  (5) Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.1$  (1),  $D_x = 1.102$  (2) Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å for graphite-monochromatized radiation,  $\mu(\text{Mo } K\alpha) = 0.071$  mm<sup>-1</sup>,  $T = 140$  K,  $F(000) = 816$ ,  $R = 0.045$  for 1330 unique reflections. Bis[*N*<sup>1</sup>-(2,2-dimethylpropionyl)-2,2-dimethylpropionamidyl] disulfate (*N*-pivaloylamidinium pyrosulfate), 2C<sub>10</sub>H<sub>21</sub>N<sub>2</sub>O<sup>+</sup>·S<sub>2</sub>O<sub>7</sub><sup>2-</sup> (III):  $M_r = 546.71$ , triclinic,  $P1$ ,  $a = 9.628$  (2),  $b = 10.457$  (2),  $c = 14.964$  (3) Å,  $\alpha = 76.25$  (2),  $\beta = 72.86$  (2),  $\gamma = 86.14$  (2)°,  $V = 1398.3$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.3$  (1),  $D_x = 1.298$  (5) Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å for graphite-monochromatized radiation,  $\mu(\text{Mo } K\alpha) = 0.231$  mm<sup>-1</sup>,  $T = 140$  K,  $F(000) = 588$ ,  $R = 0.046$  for 3128 unique reflections. *N*<sup>2</sup>-(2,2-Dimethylpropionyl)-2,2-dimethylpropionamide (*N*-pivaloylpivalamide), C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>O (IV):  $M_r = 184.28$ , monoclinic,  $P2_1/a$ ,  $a = 11.603$  (6),  $b = 17.277$  (11),  $c = 12.103$  (8) Å,  $\beta = 106.35$  (5)°,  $V = 2328$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.0$  (1),  $D_x = 1.051$  (1) Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å for graphite-monochromatized radiation,  $\mu(\text{Mo } K\alpha) = 0.064$  mm<sup>-1</sup>,  $T = 140$  K,  $F(000) = 816$ ,  $R = 0.063$  for 1914 unique reflections. In these compounds, all of which contain nominally *sp*<sup>2</sup>-hybridized C,N,O frameworks, CN bonds span the range 1.281 (4)–1.409 (4) Å. Resonance structures are proposed with unequal weightings that rationalize the observed geometrical variations. Among the eleven different *tert*-butyl (*t*-Bu) groups encountered, eight adopt configurations having a methyl C atom nearly coplanar with the adjacent *sp*<sup>2</sup> centers. The central NH group in (II) and (III), and the central N in (IV) are shielded by the *t*-Bu groups and are not H-bonded. In (III) and (IV) both inter- and intramolecular NH...O hydrogen bonds are formed by the NH<sub>2</sub> groups. Only intermolecular H bonds occur in (I).

**Introduction.** Almost a century ago, in a paper that has gone largely unnoticed, Eitner (1893) reported the precipitation of a crystalline compound from a reaction mixture that contained acetonitrile and fuming sulfuric acid. This product hydrolyzed readily to form *N*-acetylacetamide (diacetamide) and sulfamic acid. An X-ray study by Hope & Nichols (1981) established that Eitner's original compound is *N*-[1-(acetylamino)-ethylidene]sulfamic acid zwitterion. The present paper reports some of the results of experiments intended to explore the scope of nitrile-oleum reactions.

**Experimental.** The current compounds were synthesized in the order (III), (IV), (II), (I). Compound (III) was prepared by the dropwise addition of 1 mL of 20% fuming sulfuric acid to 10 mL of 2,2-dimethylpropionitrile (pivalonitrile). After an hour, 40 mL of ethyl acetate was added, causing an oil to separate. The oil slowly deposited large, colorless crystals of (III) which were collected, washed with ethyl acetate, and

dried *in vacuo*. Prompt neutralization of an aqueous solution of (III) with NaHCO<sub>3</sub> gave crude (IV). Crystallographic samples were prepared by the slow evaporation of a cyclohexane solution of the crude product. Suitable crystals of the insoluble compound (II) formed slowly when (III) was dissolved in a small amount of water. The very acidic solution contained sulfate, but no sulfamic acid could be detected by the usual NaNO<sub>2</sub> test. A crude sample of (II) was found to have hydrolyzed spontaneously to (I) after 6 months storage in a humid environment. The resulting product was recrystallized from water.

Colorless single crystals of compounds (I)–(IV) were mounted on a computer-controlled Nicolet *P2*<sub>1</sub> diffractometer. Densities measured by flotation methods. Crystal sizes 0.12 × 0.37 × 0.48 (I); 0.10 × 0.20 × 0.95 (II); 0.25 × 0.38 × 0.63 (III); 0.08 × 0.18 × 0.55 (IV) mm, respectively. Cell constants determined by least-squares refinements from 15 individual reflections that span the ranges 8° < 2θ < 21.4° (I); 7.5° < 2θ < 15.9° (II); 6° < 2θ < 21.9° (III); 5.9° < 2θ < 18.8° (IV), respectively. For the collection of intensities we used ω-scan modes with the following scan speed (° min<sup>-1</sup>): 10 (I); 6–60 (II); 60 (III); 10 (IV), respectively, and the ranges of *hkl* were for (I) 0→14, 0→8, -14→14; (II) 0→15, 0→16, 0→24; (III) 0→11, -13→13, -17→17; (IV) 0→15, 0→23, -16→16. For each crystal two standard reflections were measured with intervals of 198 observations. The scan ranges (°) were 1.6 (I); 1.0 (II); 1.0 (III); 1.2 (IV), with a background to scan time ratio of 1.0. The respective numbers of measured unique reflections were 1636 (I), 2922 (II), 5248 (III), 5343 (IV), as data were collected below 55° in 2θ for (I), (II) and (IV) and below 50° for (III).  $R_{\text{merge}} = 0.008$  (I), 0.025 (II), 0.018 (III), 0.063 (IV).

For the structure analyses the data were restricted by excluding reflections with *F* values smaller than  $n\sigma(F)$  where  $n = 4$  for (I) and 6 for (II), (III) and (IV). The number of unique structure factors used finally became 1035 (I), 1339 (II), 3128 (III) and 1914 (IV). The two test reflections were stable during the data collections at 140 K, and the intensity data were reduced according to standard procedures in the Nicolet software. No corrections for absorption were applied. The atomic scattering factors including anomalous-dispersion effects were from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a Data General Eclipse computer, using the *SHELXTL* (Sheldrick, 1981) program system. The structures were solved by direct methods, and the refinements were by least-squares calculations.  $\sum w(|F_o| - |F_c|)^2$  minimized with weighting schemes based on trends in  $w\Delta^2$  versus  $F_o$  and  $\sin\theta/\lambda$  where  $w = 1/[\sigma^2(F) + GF^2]$ .  $G$  was  $1 \times 10^{-4}$  (I),  $1 \times 10^{-3}$  (II),  $5 \times 10^{-4}$  (III) and 0.000 for (IV), respectively. The final agreement factors (*R*) and goodness-of-fit values (*S*) were as follows: (I): *R*

= 0.044,  $wR = 0.041$ ,  $S = 1.620$ ; (II):  $R = 0.045$ ,  $wR = 0.049$ ,  $S = 1.144$ ; (III):  $R = 0.046$ ,  $wR = 0.047$ ,  $S = 1.243$ ; (IV):  $R = 0.064$ ,  $wR = 0.048$ ,  $S = 1.391$ . In final least-squares cycle  $(\Delta/\sigma)_{\max} = 0.009$  (I), 0.022 (II), 0.70 (III), 0.71 (IV) for nonhydrogen-atom parameters.  $\Delta\rho$  excursions were less than 0.50 to  $-0.40 \text{ e } \text{\AA}^{-3}$  for all the structures. For the structure of pivalamide (I) the space group  $P2_1$  represented a possible alternative to  $P2_1/a$  because two 'forbidden' reflections, 101 and 303, were observed. Refinement in  $P2_1$  terminated with  $R = 3.4\%$ , but gave unacceptable values for bond distances and angles in the two independent molecules. The two weak reflections hence were thought to be caused by Renninger effects and excluded from the calculations, leaving us with the space group  $P2_1/a$  and reasonable molecular dimensions.

For all structures in this paper, the heavy atoms were refined using anisotropic thermal parameters, whereas the H atoms were included with isotropic values.

**Discussion.** The positional coordinates for these structures are given in Tables 1–4. Bond lengths, bond angles, torsion angles and hydrogen-bond relations are given in Tables 5–8.\*

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distances involving H atoms, torsion angles and H-bond data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42586 (65 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Pivalamide (I): fractional atomic coordinates ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>*</sup>
O(1)	-661 (1)	3077 (2)	6061 (1)	27 (1)
N	1454 (1)	3206 (2)	5834 (1)	23 (1)
C(1)	511 (1)	2426 (3)	6412 (1)	19 (1)
C(2)	921 (1)	783 (3)	7568 (2)	20 (1)
C(3)	2085 (2)	-725 (4)	7432 (2)	41 (1)
C(4)	-260 (2)	-724 (4)	7658 (2)	39 (1)
C(5)	1301 (3)	2249 (4)	8809 (2)	46 (1)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 2. *Dipivalamide (II): fractional atomic coordinates ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>*</sup>
N	6615 (2)	7988 (2)	6213 (1)	26 (1)
O(1)	8530 (1)	7406 (2)	5858 (1)	32 (1)
O(2)	7941 (2)	8921 (2)	6989 (1)	64 (1)
C(1)	7448 (2)	7504 (2)	5713 (1)	23 (1)
C(2)	6903 (2)	7130 (2)	4956 (1)	23 (1)
C(3)	6339 (3)	8195 (2)	4573 (2)	32 (1)
C(4)	7921 (2)	6641 (2)	4464 (1)	36 (1)
C(5)	5923 (2)	6196 (2)	5077 (1)	34 (1)
C(6)	6901 (2)	8686 (2)	6834 (1)	31 (1)
C(7)	5790 (2)	9143 (2)	7267 (1)	26 (1)
C(8)	5053 (4)	8133 (3)	7593 (2)	43 (1)
C(9)	4968 (2)	9861 (2)	6741 (1)	27 (1)
C(10)	6249 (3)	9925 (3)	7906 (2)	43 (1)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 3. *N-Pivaloylpivalamidinium pyrosulfate (III): fractional atomic coordinates ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>*</sup>
S(1)	7613 (1)	2137 (1)	7528 (1)	25 (1)
S(2)	10394 (1)	852 (1)	6983 (1)	31 (1)
O(1)	8572 (3)	862 (2)	7282 (2)	29 (1)
O(11)	7725 (3)	3046 (2)	6626 (2)	33 (1)
O(12)	8232 (3)	2645 (2)	8148 (2)	29 (1)
O(13)	6201 (3)	1556 (2)	7994 (2)	35 (1)
O(21)	10848 (3)	2128 (2)	6376 (2)	38 (1)
O(22)	10700 (3)	-213 (3)	6499 (2)	47 (1)
O(23)	10701 (3)	566 (3)	7892 (2)	42 (1)
C(1)	2037 (4)	2245 (3)	9275 (2)	25 (1)
C(2)	2465 (4)	3542 (3)	8554 (2)	27 (1)
C(21)	3146 (5)	3378 (4)	7520 (3)	45 (2)
C(22)	3604 (4)	4156 (4)	8847 (3)	43 (2)
C(23)	1118 (4)	4413 (4)	8620 (3)	51 (2)
O(2)	1120 (3)	2137 (2)	10033 (2)	40 (1)
N(1)	2815 (3)	1137 (3)	9026 (2)	24 (1)
N(2)	1674 (3)	-404 (3)	10362 (2)	25 (1)
C(3)	2605 (3)	-117 (3)	9531 (2)	21 (1)
C(4)	3513 (4)	-1200 (3)	9108 (3)	29 (1)
C(41)	4819 (5)	-1454 (4)	9521 (3)	45 (2)
C(42)	2596 (7)	-2438 (5)	9400 (4)	76 (3)
C(43)	4069 (4)	-782 (4)	8021 (3)	33 (1)
C(5)	12363 (4)	-3444 (3)	5543 (2)	20 (1)
C(6)	13585 (4)	-2457 (3)	5317 (2)	24 (1)
C(61)	13706 (4)	-2252 (3)	6270 (3)	31 (1)
C(62)	13269 (4)	-1153 (3)	4698 (3)	32 (1)
C(63)	14993 (4)	-3059 (4)	4796 (3)	46 (2)
O(3)	12545 (2)	-4540 (2)	5390 (2)	26 (1)
N(3)	10969 (3)	-3028 (2)	6005 (2)	23 (1)
N(4)	9769 (3)	-4959 (3)	6212 (2)	27 (1)
C(7)	9733 (4)	-3765 (3)	6323 (2)	22 (1)
C(8)	8354 (4)	-3138 (3)	6819 (3)	28 (1)
C(81)	7054 (4)	-4051 (4)	7083 (3)	43 (2)
C(82)	8092 (4)	-1855 (3)	6132 (3)	33 (1)
C(83)	8536 (4)	-2840 (4)	7735 (3)	37 (2)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 4. *N-Pivaloylpivalamide (IV): fractional atomic coordinates ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>*</sup>
O(1)	3269 (3)	4429 (2)	2712 (2)	29 (1)
N(1)	3787 (3)	3749 (2)	1257 (3)	18 (1)
N(2)	4513 (3)	3163 (2)	3078 (3)	24 (1)
C(1)	3242 (4)	4335 (3)	1691 (4)	20 (2)
C(2)	2567 (4)	4916 (2)	788 (4)	20 (2)
C(21)	1812 (4)	5453 (3)	1309 (4)	37 (2)
C(22)	3522 (4)	5384 (3)	408 (4)	33 (2)
C(23)	1772 (4)	4491 (2)	-256 (4)	30 (2)
C(3)	4379 (4)	3209 (2)	1960 (3)	18 (2)
C(4)	5009 (4)	2567 (2)	1445 (3)	17 (2)
C(41)	4689 (4)	2646 (3)	140 (4)	33 (2)
C(42)	6381 (4)	2655 (2)	1964 (4)	29 (2)
C(43)	4603 (4)	1765 (2)	1750 (4)	29 (2)
O(2)	925 (3)	2883 (2)	4775 (2)	31 (1)
N(3)	1554 (3)	3876 (2)	6120 (3)	20 (1)
N(4)	2075 (3)	4096 (2)	4401 (3)	25 (1)
C(5)	1011 (4)	3186 (3)	5730 (4)	23 (2)
C(6)	518 (4)	2771 (2)	6616 (4)	22 (2)
C(61)	-249 (4)	3332 (3)	7087 (4)	33 (2)
C(62)	-245 (5)	2076 (3)	6081 (4)	58 (3)
C(63)	1589 (4)	2507 (3)	7597 (4)	46 (2)
C(7)	2033 (4)	4294 (2)	5446 (3)	19 (2)
C(8)	2573 (4)	5074 (2)	5933 (4)	22 (2)
C(81)	1538 (4)	5562 (3)	6126 (4)	34 (2)
C(82)	3155 (4)	5507 (2)	5122 (4)	29 (2)
C(83)	3524 (4)	4927 (3)	7087 (4)	32 (2)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

After some general observations applicable to all of them, two aspects of the structures of each compound will be discussed: namely, the dispositions of the *t*-Bu groups and the bonding in the frameworks to which they are attached.

This set of compounds yielded eleven different *t*-Bu-group structures. In every instance the methyl groups were arranged around the central C atom in such a way that HCCC torsion-angle magnitudes of 60 (5) or 175 (5)° were found. That is, the H atoms on adjacent methyl groups are eclipsed, with closest H...H separations of about 2.5 Å. Within the *t*-Bu groups the Me—C—Me bond angles range from 108.0 to 110.8°,

Table 5. *Pivalamide* (I): bond lengths (Å), bond angles (°), selected torsion angles (°) and hydrogen-bond lengths (Å)

E.s.d.'s are in parentheses. A minus sign indicates anticlockwise rotation.

O(1)—C(1)	1.243 (2)	N—C(1)	1.331 (2)
C(1)—C(2)	1.530 (2)	C(2)—C(3)	1.524 (3)
C(2)—C(4)	1.526 (3)	C(2)—C(5)	1.531 (3)
O(1)—C(1)—N	121.3 (1)	O(1)—C(1)—C(2)	120.6 (1)
N—C(1)—C(2)	118.1 (1)	C(1)—C(2)—C(3)	112.6 (2)
C(1)—C(2)—C(4)	109.3 (1)	C(3)—C(2)—C(4)	108.7 (2)
C(1)—C(2)—C(5)	106.3 (1)	C(3)—C(2)—C(5)	110.3 (2)
C(4)—C(2)—C(5)	109.7 (2)		
O(1)—C(1)—C(2)—C(5)	-88.8 (2)	N—C(1)—C(2)—C(4)	-153.3 (2)
N—C(1)—C(2)—C(5)	88.4 (2)	O(1)—C(1)—C(2)—C(3)	150.4 (2)
N—C(1)—C(2)—C(3)	-32.4 (2)	O(1)—C(1)—C(2)—C(4)	29.5 (2)
Hydrogen bond	H...O	N...O	O atom symmetry code
N—H1N...O(1)	2.06	2.942	-x, 1-x, 1-z
N—H2N...O(1)	3.03	3.026	‡+x, †-y, z

Table 6. *Dipivalamide* (II): bond lengths (Å), selected bond angles (°) and torsion angles (°)

E.s.d.'s are in parentheses. A minus sign indicates anticlockwise rotation.

N—C(1)	1.388 (3)	N—C(6)	1.400 (3)
O(1)—C(1)	1.211 (3)	O(2)—C(6)	1.197 (3)
C(1)—C(2)	1.532 (3)	C(2)—C(3)	1.533 (3)
C(2)—C(4)	1.520 (3)	C(2)—C(5)	1.533 (3)
C(6)—C(7)	1.529 (3)	C(7)—C(8)	1.530 (4)
C(7)—C(9)	1.536 (3)	C(7)—C(10)	1.534 (4)
C(1)—N—C(6)	126.2 (2)	N—C(1)—O(1)	122.5 (2)
N—C(1)—C(2)	115.0 (2)	O(1)—C(1)—C(2)	122.5 (2)
C(1)—C(2)—C(3)	108.6 (2)	C(1)—C(2)—C(4)	109.0 (2)
C(3)—C(2)—C(4)	109.6 (2)	C(1)—C(2)—C(5)	110.1 (2)
C(3)—C(2)—C(5)	110.4 (2)	C(4)—C(2)—C(5)	109.1 (2)
N—C(6)—O(2)	121.4 (2)	N—C(6)—C(7)	114.8 (2)
O(2)—C(6)—C(7)	123.7 (2)	C(6)—C(7)—C(8)	110.1 (2)
C(6)—C(7)—C(9)	109.9 (2)	C(8)—C(7)—C(9)	109.7 (2)
C(6)—C(7)—C(7)	108.6 (2)	C(8)—C(7)—C(10)	109.8 (2)
C(9)—C(7)—C(10)	108.8 (2)		
C(6)—N—C(1)—O(1)	18.1 (4)	O(1)—C(1)—C(2)—C(3)	-119.0 (2)
C(6)—N—C(1)—C(2)	-160.5 (2)	O(1)—C(1)—C(2)—C(4)	0.3 (3)
C(1)—N—C(6)—O(2)	-0.7 (4)	O(1)—C(1)—C(2)—C(5)	120.0 (2)
C(1)—N—C(6)—C(7)	177.4 (2)	N—C(6)—C(7)—C(9)	-58.9 (2)
N—C(1)—C(2)—C(3)	59.6 (3)	N—C(6)—C(7)—C(10)	-177.9 (3)
N—C(1)—C(2)—C(4)	179.0 (2)	O(2)—C(6)—C(7)—C(8)	-120.0 (3)
N—C(1)—C(2)—C(5)	-61.4 (3)	O(2)—C(6)—C(7)—C(9)	119.1 (3)
O(2)—C(6)—C(7)—C(10)	0.2 (3)		

with a mean value of 109.7 (6)°. The Me—C bond lengths range from 1.517 to 1.545 Å with a mean value of 1.530 (8) Å. The average C—H bond length based on 99 individual observations is 0.99 (3) Å.

Table 7. *N-Pivaloylpivalamidinium pyrosulfate* (III): bond lengths (Å), bond angles (°), selected torsion angles (°) and hydrogen-bond lengths (Å)

E.s.d.'s are in parentheses. A minus sign indicates anticlockwise rotation.

S(1)—O(1)	1.622 (2)	S(1)—O(11)	1.434 (2)
S(1)—O(12)	1.450 (3)	S(1)—O(13)	1.433 (2)
S(2)—O(1)	1.678 (2)	S(2)—O(21)	1.437 (2)
S(2)—O(22)	1.437 (3)	S(2)—O(23)	1.435 (3)
C(1)—C(2)	1.514 (4)	C(1)—O(2)	1.201 (4)
C(1)—N(1)	1.401 (4)	C(2)—C(21)	1.538 (5)
C(2)—C(22)	1.523 (6)	C(2)—C(23)	1.527 (5)
N(1)—C(3)	1.344 (4)	N(2)—C(3)	1.281 (4)
C(3)—C(4)	1.527 (5)	C(4)—C(41)	1.540 (6)
C(4)—C(42)	1.518 (6)	C(4)—C(43)	1.517 (5)
C(5)—C(6)	1.526 (5)	C(5)—O(3)	1.212 (4)
C(5)—N(3)	1.409 (4)	C(6)—C(61)	1.530 (6)
C(6)—C(62)	1.524 (5)	C(6)—C(63)	1.529 (5)
N(3)—C(7)	1.361 (4)	N(4)—C(7)	1.295 (5)
C(7)—C(8)	1.509 (4)	C(8)—C(81)	1.525 (5)
C(8)—C(82)	1.540 (5)	C(8)—C(83)	1.535 (6)
O(1)—S(1)—O(11)	106.4 (1)	O(1)—S(1)—O(12)	106.6 (1)
O(11)—S(1)—O(12)	113.0 (1)	O(1)—S(1)—O(13)	101.1 (1)
O(11)—S(1)—O(13)	114.1 (2)	O(12)—S(1)—O(13)	114.3 (2)
O(1)—S(2)—O(21)	105.7 (1)	O(1)—S(2)—O(22)	100.2 (2)
O(21)—S(2)—O(22)	114.9 (2)	O(1)—S(2)—O(23)	103.7 (1)
O(21)—S(2)—O(23)	115.7 (2)	O(22)—S(2)—O(23)	114.2 (2)
S(1)—O(1)—S(2)	122.7 (2)	C(2)—C(1)—O(2)	123.8 (3)
C(2)—C(1)—N(1)	116.0 (3)	O(2)—C(1)—N(1)	120.2 (3)
C(1)—C(2)—C(21)	113.0 (3)	C(1)—C(2)—C(22)	106.4 (3)
C(21)—C(2)—C(22)	108.0 (3)	C(1)—C(2)—C(23)	108.2 (3)
C(21)—C(2)—C(23)	110.8 (3)	C(22)—C(2)—C(23)	110.4 (3)
C(1)—N(1)—C(3)	127.0 (2)	N(1)—C(3)—N(2)	120.9 (3)
N(1)—C(3)—C(4)	119.0 (3)	N(2)—C(3)—C(4)	120.2 (3)
C(3)—C(4)—C(41)	107.2 (3)	C(3)—C(4)—C(42)	109.2 (3)
C(41)—C(4)—C(42)	110.2 (4)	C(3)—C(4)—C(43)	111.3 (3)
C(41)—C(4)—C(43)	109.0 (3)	C(42)—C(4)—C(43)	109.9 (4)
C(6)—C(5)—O(3)	124.2 (3)	C(6)—C(5)—N(3)	115.2 (3)
O(3)—C(5)—N(3)	120.6 (3)	C(5)—C(6)—C(61)	107.9 (2)
C(5)—C(6)—C(62)	110.7 (3)	C(61)—C(6)—C(62)	110.1 (3)
C(5)—C(6)—C(63)	107.7 (3)	C(61)—C(6)—C(63)	109.6 (3)
C(62)—C(6)—C(63)	110.7 (3)	C(5)—N(3)—C(7)	125.7 (3)
N(3)—C(7)—N(4)	120.4 (3)	N(3)—C(7)—C(8)	117.1 (3)
N(4)—C(7)—C(8)	122.5 (3)	C(7)—C(8)—C(81)	111.0 (3)
C(7)—C(8)—C(82)	108.7 (3)	C(81)—C(8)—C(82)	108.8 (3)
C(7)—C(8)—C(88)	108.7 (3)	C(81)—C(8)—C(83)	109.5 (3)
C(82)—C(8)—C(88)	110.3 (3)		
O(11)—S(1)—O(1)—S(2)	76.5 (2)	O(3)—C(5)—C(6)—C(61)	-113.0 (4)
O(21)—S(2)—O(1)—S(1)	-39.3 (2)	N(3)—C(5)—C(6)—C(61)	63.4 (4)
O(2)—C(1)—C(2)—C(21)	-156.1 (4)	O(3)—C(5)—C(6)—C(62)	126.4 (4)
N(1)—C(1)—C(2)—C(21)	26.0 (5)	N(3)—C(5)—C(6)—C(62)	-57.2 (4)
C(2)—C(1)—N(1)—C(3)	-177.8 (4)	N(1)—C(3)—C(4)—C(41)	95.3 (4)
O(12)—S(1)—O(1)—S(2)	-44.3 (2)	N(2)—C(3)—C(4)—C(41)	-83.7 (4)
O(22)—S(2)—O(1)—S(1)	-159.0 (2)	N(1)—C(3)—C(4)—C(42)	-145.3 (4)
O(2)—C(1)—C(2)—C(22)	85.6 (5)	N(2)—C(3)—C(4)—C(42)	35.7 (6)
N(1)—C(1)—C(2)—C(22)	-92.3 (4)	N(3)—C(7)—C(8)—C(81)	176.8 (3)
O(13)—S(1)—O(1)—S(2)	-164.0 (2)	N(4)—C(7)—C(8)—C(81)	-4.4 (5)
O(23)—S(2)—O(1)—S(1)	82.8 (2)	N(3)—C(7)—C(8)—C(82)	57.2 (4)
O(2)—C(1)—C(2)—C(23)	-33.0 (6)	N(4)—C(7)—C(8)—C(82)	-124.0 (4)
N(1)—C(1)—C(2)—C(23)	149.1 (4)	C(1)—N(1)—C(3)—N(2)	-4.6 (6)
C(2)—C(1)—N(1)—C(3)	4.2 (6)	N(3)—C(7)—C(8)—C(83)	-62.8 (4)
O(3)—C(5)—C(6)—C(63)	5.2 (5)	N(4)—C(7)—C(8)—C(83)	116.0 (4)
N(3)—C(5)—C(6)—C(63)	-178.4 (3)	C(5)—N(3)—C(7)—N(4)	-0.1 (5)
N(1)—C(3)—C(4)—C(43)	-23.8 (5)	C(5)—N(3)—C(7)—C(8)	178.7 (3)
N(2)—C(3)—C(4)—C(43)	157.3 (4)		
C(1)—N(1)—C(3)—C(4)	176.4 (4)		
Hydrogen bond	H...O	N...O	O atom symmetry code
N(2)—HN2A...O(2)	1.983	2.633	x, y, z
N(2)—HN2B...O(12)	2.046	2.842	1-x, -y, 2-z
N(4)—HN4A...O(3)	1.936	2.610	x, y, z
N(4)—HN4B...O(11)	1.947	2.798	x, -1+y, z

Table 8. *N*-Pivaloylpivalamidine (IV): bond lengths (Å), bond angles (°), selected torsion angles (°) and hydrogen-bond lengths (Å)

E.s.d.'s are in parentheses. A minus sign indicates anticlockwise rotation.

O(1)—C(1)	1.238 (5)	N(1)—C(1)	1.374 (6)
N(1)—C(3)	1.318 (5)	N(2)—C(3)	1.320 (5)
C(1)—C(2)	1.527 (6)	C(2)—C(21)	1.529 (7)
C(2)—C(22)	1.544 (7)	C(2)—C(23)	1.526 (5)
C(3)—C(4)	1.552 (6)	C(4)—C(41)	1.523 (6)
C(4)—C(42)	1.545 (6)	C(4)—C(43)	1.541 (6)
O(2)—C(5)	1.247 (5)	N(3)—C(5)	1.368 (5)
N(3)—C(7)	1.323 (6)	N(4)—C(7)	1.324 (6)
C(5)—C(6)	1.528 (7)	C(6)—C(61)	1.531 (7)
C(6)—C(62)	1.523 (6)	C(6)—C(63)	1.527 (6)
C(7)—C(8)	1.533 (6)	C(8)—C(81)	1.538 (7)
C(8)—C(82)	1.532 (7)	C(8)—C(83)	1.538 (5)
C(1)—N(1)—C(3)	119.1 (4)	O(1)—C(1)—N(1)	126.4 (4)
O(1)—C(1)—C(2)	119.5 (4)	N(1)—C(1)—C(2)	114.1 (4)
C(1)—C(2)—C(21)	110.0 (4)	C(1)—C(2)—C(22)	107.0 (3)
C(21)—C(2)—C(22)	110.3 (3)	C(1)—C(2)—C(23)	110.2 (3)
C(21)—C(2)—C(23)	110.5 (3)	C(22)—C(2)—C(23)	108.8 (4)
N(1)—C(3)—N(2)	126.4 (4)	N(1)—C(3)—C(4)	117.7 (4)
N(2)—C(3)—C(4)	115.9 (3)	C(3)—C(4)—C(41)	110.3 (3)
C(3)—C(4)—C(42)	108.3 (3)	C(41)—C(4)—C(42)	109.6 (4)
C(3)—C(4)—C(43)	109.6 (4)	C(41)—C(4)—C(43)	109.1 (3)
C(42)—C(4)—C(43)	109.9 (3)	C(5)—N(3)—C(7)	119.7 (4)
O(2)—C(5)—N(3)	126.4 (4)	O(2)—C(5)—C(6)	120.4 (4)
N(3)—C(5)—C(6)	113.2 (4)	C(5)—C(6)—C(61)	109.7 (4)
C(5)—C(6)—C(62)	111.0 (4)	C(61)—C(6)—C(62)	109.2 (4)
C(5)—C(6)—C(63)	107.6 (4)	C(61)—C(6)—C(63)	109.3 (4)
C(62)—C(6)—C(63)	110.1 (4)	N(3)—C(7)—N(4)	125.6 (4)
N(3)—C(7)—C(8)	116.1 (4)	N(4)—C(7)—C(8)	118.2 (4)
C(7)—C(8)—C(81)	106.8 (3)	C(7)—C(8)—C(82)	112.9 (4)
C(81)—C(8)—C(82)	109.5 (3)	C(7)—C(8)—C(83)	108.4 (3)
C(81)—C(8)—C(83)	110.1 (4)	C(82)—C(8)—C(83)	109.2 (4)
N(1)—C(3)—C(4)—C(41)	-6.3 (5)	N(3)—C(7)—C(8)—C(81)	-62.0 (4)
N(2)—C(3)—C(4)—C(42)	174.8 (4)	N(4)—C(7)—C(8)—C(81)	117.6 (4)
N(1)—C(3)—C(4)—C(43)	113.6 (4)	N(3)—C(7)—C(8)—C(82)	177.7 (3)
N(2)—C(3)—C(4)—C(43)	-65.3 (5)	N(4)—C(7)—C(8)—C(82)	-2.8 (5)
N(1)—C(3)—C(4)—C(43)	-126.5 (4)	N(3)—C(7)—C(8)—C(83)	56.5 (5)
N(2)—C(3)—C(4)—C(43)	54.6 (4)	N(4)—C(7)—C(8)—C(83)	-123.9 (4)
C(1)—N(1)—C(3)—N(2)	0.2 (6)	C(5)—N(3)—C(7)—N(4)	-2.1 (6)
O(1)—C(1)—C(2)—C(22)	108.7 (4)	O(2)—C(5)—C(6)—C(62)	-10.8 (6)
N(1)—C(1)—C(2)—C(22)	-70.4 (4)	N(3)—C(5)—C(6)—C(62)	171.0 (4)
C(3)—N(1)—C(1)—C(2)	-179.0 (4)	C(7)—N(3)—C(5)—C(6)	179.3 (3)
O(1)—C(1)—C(2)—C(21)	-11.1 (5)	O(2)—C(5)—C(6)—C(61)	-131.5 (4)
N(1)—C(1)—C(2)—C(21)	169.8 (3)	N(3)—C(5)—C(6)—C(61)	50.3 (4)
C(3)—N(1)—C(1)—O(1)	2.0 (6)	C(7)—N(3)—C(5)—O(2)	1.2 (6)
C(1)—N(1)—C(3)—O(4)	-178.6 (8)	C(5)—N(3)—C(7)—C(8)	177.4 (3)
O(1)—C(1)—C(2)—C(23)	-133.2 (4)	O(2)—C(5)—C(6)—C(63)	109.7 (4)
N(1)—C(1)—C(2)—C(23)	47.8 (5)	N(3)—C(5)—C(6)—C(63)	-68.5 (5)

Hydrogen bond	O atom		
	H...O	N...O	symmetry code
N(2)—H2N...O(1)	1.874	2.588	<i>x, y, z</i>
N(2)—H2NB...O(2)	2.076	2.878	$\frac{1}{2}+x, \frac{1}{2}-y, z$
N(4)—H4NA...O(2)	1.856	2.591	<i>x, y, z</i>
N(4)—H4NB...O(1)	2.016	2.833	<i>x, y, z</i>

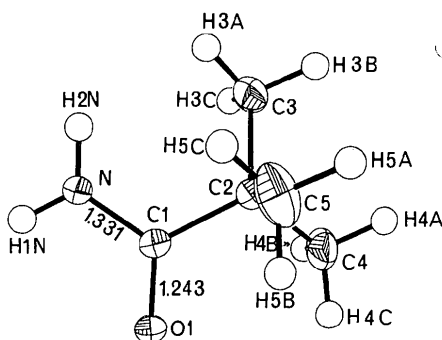


Fig. 1. Perspective drawing of pivalamide (I) with significant bond distances (Å). Thermal ellipsoids are at 50% probability for non-hydrogen atoms.

*2,2-Dimethylpropionamide*. Compound (I), which we will call by its trivial name pivalamide, is shown in Fig. 1. It has a planar group of atoms C(2), C(1), O(1), NH<sub>2</sub> that is virtually perpendicular to another planar group defined by atoms C(1), C(2), C(5), H(5A). This 'clinal' conformation is different from the 'periplanar' ones in propionamide (Usanmaz & Adler, 1982) where the methyl C atom is *syn* to the carbonyl O, or in 2-methylpropionamide (Cohen-Addad & Cohen-Addad, 1978) where the methine H atom is *anti* to the carbonyl O. Torsion angles similar to the present ones were found for the methylene C and the methine H atoms in 2-ethylbutyramide (Cohen-Addad, 1979). A less regular orientation was observed in *N*-pivaloyl-D-alanyl-L-proline-*N*-isopropylamide (Aubry, Protas, Boussard & Marraud, 1979). We presume that crystal packing and H-bonding requirements will largely govern the rotatory positioning of the alkyl groups in all these crystals.

The bond lengths and bond angles in the amide group differ only slightly from the values found in the cited compounds. It is quite apparent that atoms C(1) and N are *sp*<sup>2</sup> hybridized, and that the structure  $R-\overset{+}{C}=\overset{-}{N}H_2$

makes an appreciable contribution to the observed molecular geometry. The N atom is engaged in H bonding to C=O in two neighboring molecules.

*Bis(2,2-dimethylpropionyl)amine*. Compound (II), hereafter called dipivalamide, is shown in Fig. 2. The *t*-Bu moieties are oriented such that atoms C(4) and C(10) adopt *syn* conformations with respect to O(1) and O(2). The molecule can be described as having two planar portions, C(4), C(2), C(1), O(1), N (r.m.s.d. 0.006 Å), and C(10), C(7), C(6), O(2), N (r.m.s.d. 0.011 Å), that intersect with an angle of 18.9 (5)° between their normals. H atoms H(4C) and H(10C) are also only 0.025 and 0.040 Å out of these respective planes.

The 18.9° intersection is mainly created by a rotation about the N—C(1) bond, and is presumably caused by electrostatic repulsion between the O atoms. *Ab initio* calculations on acetamides led Radom & Riggs (1980) to conclude that this would destabilize the strictly planar *Z,Z* conformation of diacetamide

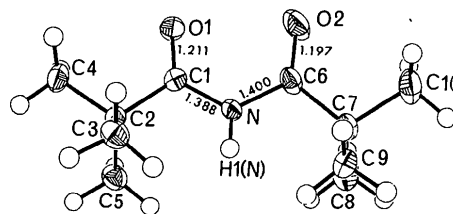
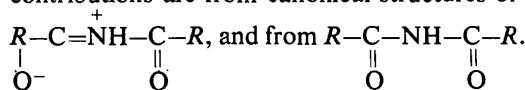


Fig. 2. Perspective drawing of dipivalamide (II) with significant bond distances (Å) and atomic labelling. Thermal ellipsoids are at 50% probability for non-hydrogen atoms.

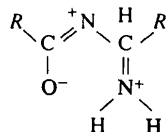
molecules. Our result is in agreement with this prediction. The H atom at N adopts an intermediate position between the intersecting planes, and calculates to be 0.11 Å out of the CNC plane. More specifically, the rotation about N—C(1) causes N—H to deviate by  $\sim 8^\circ$  from the C(7), C(6), O(2), N, C(1) plane, and by  $\sim 11^\circ$  from the N, C(1), C(2), O(1) plane. The strict planarity of the C, NH, C atoms required for pure  $sp^2$  hybridization at N is thus violated, but the sum of the angles between the substituents at N is close to  $360^\circ$ . This allows for only minor elements of pyramidality at N. Nevertheless, the carbonyl bond distances closely approximate that of a pure CO double bond, and the CN bonds are considerably longer than their counterpart in (I). It is therefore an open question how large the contributions are from canonical structures of the type



In a search for comparisons we found only a relatively imprecise (e.s.d.'s 0.02 Å,  $1^\circ$ ) structure determination for diacetamide in the *Z,Z* conformation (Kuroda, Taira, Uno & Osaki, 1975). More precise structures have been established, however, for several of its ion-dipole coordination complexes. One such, the 5:1 complex with  $CaClO_4$  (Roux & Kruger, 1976), contains four coordinated diacetamide molecules having *Z,Z* conformations and one uncoordinated diacetamide molecule in an *E,Z* conformation. The average dimensions of the coordinated ones [CO 1.210 (7), CN 1.387 (6) Å, OCN 123.7 (6), CCO 122.0 (6), CNC 125.2 (7) $^\circ$ ] are quite similar to those of dipivalamide. No information is given about the H atoms.

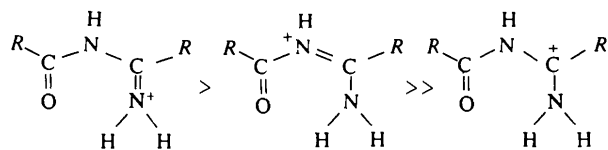
It should be noted that although the NH...O sequence in two adjacent molecules in the crystal is almost linear, the N...O separation (3.448 Å) exceeds the value regarded as significant for a H bond. Fig. 2 shows that the proton is embedded in the hydrocarbon portion of the molecule, thus precluding H-bond formation.

*Bis*[*N*-(2,2-dimethylpropionyl)-2,2-dimethylpropionamidine] disulfate. Compound (III), shown in Fig. 3, contains two stoichiometrically identical species, *A* and *B*, that might be viewed as *N*-pivaloyl-substituted pivalamidinium ions. The torsion angles in Table 7 involving C(22) and C(41) show that, with regard to the *t*-Bu-group conformations, each end of species *A* resembles pivalamide. In *B*, C(63) and C(81) are *syn* to O(3) and N(4), respectively, and hence this conformer resembles dipivalamide. When the dimensions of the central portion of (II) and (III) are compared, one sees that the amide fragments are strikingly similar. The N(1)—C(3) and N(3)—C(7) bonds are, however, shortened by  $\sim 0.04$  Å compared to N—C bonds in (II), and by  $\sim 0.05$  Å compared to N(1)—C(1) or N(3)—C(5) within (III). Also, the C—N(H<sub>2</sub>) bond distances are somewhat larger than the 1.26–1.27 Å normally ascribed to a pure CN double bond (Williams, Peterson & Brown, 1968). We thus conclude that some electron delocalization occurs in the amidinium ion fragment, but the canonical structure



is of minimal importance. This appears to be true in spite of the fact that *A*, and especially *B*, are much less twisted species than dipivalamide.

The planarity of these cations can be enhanced both by electrostatic alignment of the internal dipoles and by intermolecular H-bond formation. The contributing resonance forms in descending order of their importance are probably



The proton denoted by *HB* on each of the NH<sub>2</sub> groups forms a H bond to either O(11) or O(12), both of which are on the same SO<sub>3</sub> group in the pyrosulfate ion. A stereoview of this aspect is shown in Fig. 4. The remaining pyrosulfate O atoms and the central NH group are all buried in hydrocarbon environments.

The pyrosulfate ion is asymmetric in that the two S atoms have different distances from the bridging O atom (1.622 and 1.678 Å), the shorter distance being associated with the H-bonded SO<sub>3</sub> group. H bonding seemingly lowers the peripheral negative charge density on the participating O atoms since the O(11)S(1)O(12) angle is the smallest of the set of six such angles, while the OSO angles these atoms make to the bridging O are the largest ones of this type. The two SO<sub>3</sub> groups adopt a quasi-staggered conformation with respect to each other, presumably to minimize electrostatic repulsion.

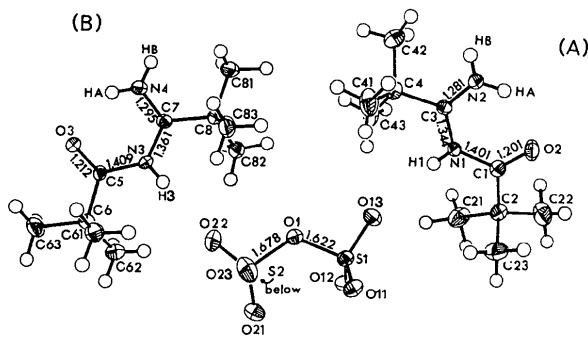


Fig. 3. Perspective drawing of the independent *N*-pivaloylpivalamidinium cations *A* and *B* and the pyrosulfate anion and a few significant bond distances (Å). Thermal ellipsoids are at 50% probability for non-hydrogen atoms.

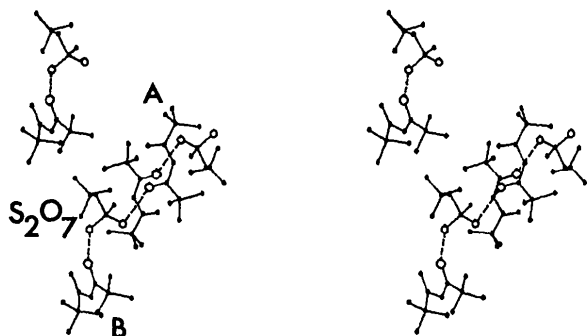


Fig. 4. Stereoview showing intermolecular hydrogen bonding in *N*-pivaloylpivalamidinium pyrosulfate (III).

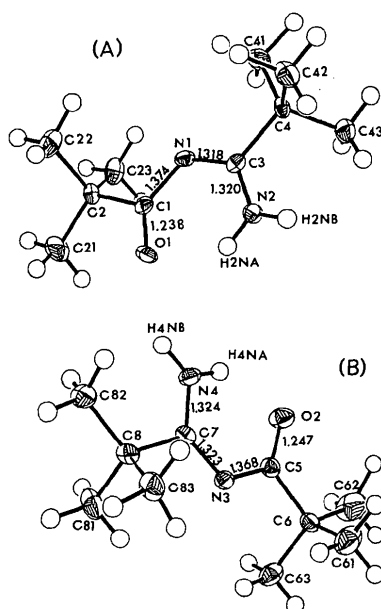


Fig. 5. Perspective drawing of the independent *N*-pivaloylpivalamidine (IV) molecules *A* and *B* with significant bond distances (Å). Thermal ellipsoids are at 50% probability for non-hydrogen atoms.

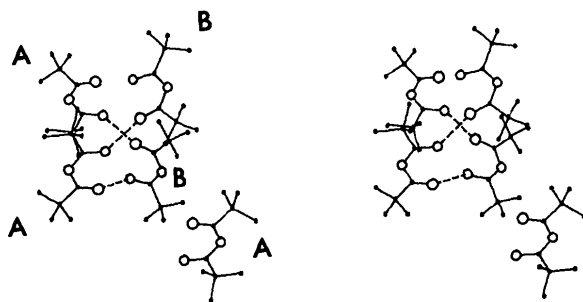
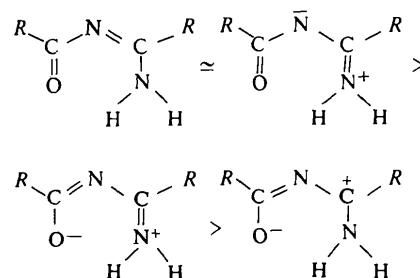


Fig. 6. Stereoview showing intermolecular hydrogen bonding in *N*-pivaloylpivalamidine (IV).

*N*<sup>2</sup>-(2,2-Dimethylpropionyl)-2,2-dimethylpropionamidine. Crystalline (IV), which is an *N*-pivaloyl-substituted pivalamidine, contains two independent molecules, *A* and *B*. As Fig. 5 shows, these differ only in the orientations of the *t*-Bu groups attached to C(NH<sub>2</sub>). In *A*, atom C(41) is *anti* to N(2), while in *B*, atom C(82) is *syn* to N(4). This 57° rotational difference in the dispositions of the two *t*-Bu groups probably results from the steric requirements of the N(2)—H<sub>2</sub>NB···O(2) hydrogen bond. The directionality of the H bond between N(4) and O(1) permits the more common *syn* configuration to be adopted in Fig. 6. In both *A* and *B*, methyl groups are *syn* to the carbonyl O atoms.

The planar skeletons of (IV), in contrast to (II) and (III), show clear evidence for electron delocalization that includes participation of the carbonyl group. Our finding that the two CN bond lengths are equal in the amidine portion of the molecule is unprecedented. In both acetamidine (Norrestam, Mertz & Crossland, 1983) and 2,6-dimethylpiperidyl-*N*-phenylacetamidine (Gilli & Bertolasi, 1979), the CN distance to the two-coordinate N atom is significantly shorter than the other one; by 0.046 and 0.096 Å, respectively.

Compared to (III), the CNC angle at the central N atom is smaller in (IV) by some 7°, reflecting the greater spatial requirements of a nonbonding electron pair. Concurrently, the NCO and NCN angles both increase by about 5.5° to accommodate the O···NH<sub>2</sub> nonbonded repulsion that would otherwise result. The participating canonical structures would seem to be



Each molecule of type *A* participates in NH···O hydrogen bonding to two molecules of type *B*, and *vice versa*. The central N atom is again shielded by the peripheral methyl groups and has no intermolecular interactions.

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## Methyl (3a*R*,4'*S*,5*R*,7*R*,7a*S*)-7-[[Cyclohexanespiro-2'-(4',5'-dihydro-2'*H*-1',3'-dioxole)]-4'-yl]-5-hydroxy-(4,5,6,7-tetrahydro-2*H*-1,3-benzodioxole)-2-spirocyclohexane-5-carboxylate

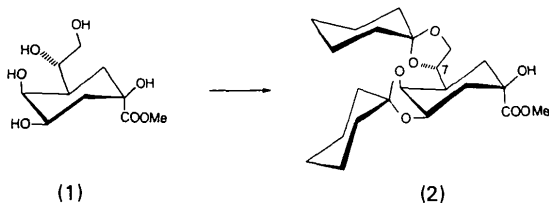
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**Abstract.** C<sub>22</sub>H<sub>34</sub>O<sub>7</sub>, *M<sub>r</sub>* = 410.506, monoclinic, *P*2<sub>1</sub>, *a* = 17.550 (8), *b* = 6.196 (1), *c* = 10.181 (3) Å, β = 98.51 (3)°, *V* = 1094.9 (6) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.245 (1) Mg m<sup>-3</sup>, λ(Cu *K*α) = 1.5406 Å, μ = 0.717 mm<sup>-1</sup>, *F*(000) = 444, room temp., *R* = 0.056 for 1415 observed reflections. The chiral centre at C(7) has *S* configuration. The molecular structure shows partial disorder. The conformation of the ester side chain is stabilized by a short (C–)H...O interaction [C...O = 3.031 (7) Å]. The crystal structure is built up of infinite chains of hydrogen-bonded molecules [O...O = 2.947 (6) Å], held together by van der Waals forces.

**Introduction.** In the course of regio- and stereoselective synthesis of the carbocyclic analogue of 3-deoxy-β-*D*-manno-2-octulopyranosic acid (β-*KDO*) from (–)-quinic acid (Molin & Pring, 1985), ester (1) was synthesized. Its structure was established by NMR spectroscopy, but the configuration at C(7) was impossible to deduce from spectroscopic data. Therefore, (1) was converted to its dicyclohexylidene derivative (2), which could be crystallized from light petroleum, for X-ray study.



**Experimental.** Intensity data collected with Philips PW 1100 diffractometer, graphite-monochromatized Cu *K*α radiation, room temp., θ limit 67° (0 ≤ *h* ≤ 21, 0 ≤ *k* ≤ 8, –13 ≤ *l* ≤ 13). Intensities of 2237 reflections (sinθ/λ<sub>max</sub> = 0.5971 Å<sup>-1</sup>) measured from colourless needle-shaped single crystal with approximate dimensions 0.003 × 0.022 × 0.004 cm. Net intensities corrected for Lorentz and polarization effects, not for absorption. 1415 reflections with σ(*I*)/*I* < 0.33 used for refinements. Unit-cell parameters refined by least-squares fitting of cell parameters to powder pattern, taken in Guinier–Hägg-type focusing camera with strictly monochromatized Cu *K*α radiation and Si (*a* = 5.4309 Å at 298 K) as internal standard. 35 line positions with 2θ < 46.5° used in the refinement. Structure solved by direct methods, using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined on *F* by full-matrix least-squares procedure of *SHELX*76 (Sheldrick, 1976) using unit weights. Structure shows partial disorder. The O(10) atom in one of the five-membered rings (*cf.* Fig. 1) had an unusually high temperature factor, and the difference electron density calculation revealed a prominent peak in its vicinity. The two positions, this peak position O(10*B*) and the former atomic site O(10*A*), were assigned partial occupancies, which refined in the following three cycles to 0.37 and 0.63, respectively. Following this adjustment the max. and min. heights in the last difference Fourier synthesis became 0.25 and –0.20 e Å<sup>-3</sup>, respectively. In the last refinement, *R* = 0.056, two positions for O(10) with individual isotropic temperature factors were refined, and