

Table I. Reduction of Carbonyl Compounds and 1,2-Oxides

Starting material	Product	% yield <sup>a</sup>
Aldehydes and Ketones		
Dodecanal	Dodecane	71 <sup>b</sup>
	Dodecanol	15-20
Decanal	Decane	61
	Decanol	11
2-Methylundecanal <i>trans</i> -2-Decenal	2-Methylundecane	44
	Decane	0-22
	1-Decene	0
<i>p</i> -Methoxybenzaldehyde	Decanol	0-5
	<i>p</i> -Cresol methyl ether	0
2-Undecanone	Undecane	3-20
	2-Undecanal	48-72
6-Dodecanone	Dodecane	7-25
	6-Dodecanol	32-70
2-Adamantanone	2-Adamantanol	72-74
Esters		
Methyl dodecanoate	Dodecane	66
	Dodecanol	9
Ethyl dodecanoate	Dodecane	64-69
	<i>trans</i> -2-Dodecene	0-4
	Dodecanol	9-14
Decyl dodecanoate	Dodecane	58
	<i>trans</i> -2-Dodecene	2
	Dodecanol	7
	Decanol	70
Methyl <i>trans</i> -2-decenoate	Decane	3-35
	1-Decene	0
	Decanol	0-2
$\gamma$ -Decalactone	4-Decanol	60
Methyl <i>trans</i> -myrtenoate	<i>trans</i> -Pinane	17
	<i>trans</i> -Myrtenol	28
Methyl 1-adamantane-carboxylate	1-Methyladamantane	0
Methyl 5 $\beta$ -cholanate	Adamantylcarbinol	35-64
	5 $\beta$ -Cholane	56 <sup>b</sup>
Methyl <i>p</i> -isopropylbenzoate	<i>p</i> -Isopropylbenzyl alcohol	82
Oxides		
1-Decene oxide	Decane	68-81
	1-Decanol	4-9
<i>trans</i> -2-Decene oxide	Decane	58
2-Methyl-1-undecene oxide	2-Methylundecane	52
$\alpha$ -Pinene oxide	<i>cis</i> -Pinane	10

<sup>a</sup> Product identity and yields were determined by gc and mass spectral methods. <sup>b</sup> Yields also based on isolated product.

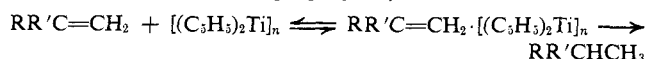
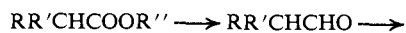
is extraordinary is revealed by reduction attempts with other transition metal species. No dodecane (or dodecene) was formed from dodecanal when the following systems were assayed:  $(C_5H_5)_2MoH_2$ ,  $(C_5H_5)_2MoH_2$ -isoprene,<sup>8</sup>  $TiH_2$ ,  $VH$ ,  $Na$ ,  $VCl_{2-3}$ - $Na$ ,  $MoCl_{3-4}$ - $Na$ . A few per cent of alkane was detected after reaction with  $(C_5H_5)_2MoH_2$  with a catalytic amount of  $HCl$ ,  $(C_5H_5)_2TaH_3$  (80°),<sup>9</sup> or  $Fe(acac)_3$ - $Na$ .

Various observations signify that the reduction of aldehydes and esters to alkanes involves olefin intermediates. Interruption of a dodecanal reaction after 3 hr revealed 10-15% 1- and 2-dodecene with 37-44% dodecane. As reaction time increased, the yield of

(8) These conditions are believed to produce a molybdenocene intermediate: B. R. Francis, M. L. H. Green, and G. G. Roberts, *Chem. Commun.*, 1290 (1971); M. L. H. Green and P. J. Knowles, *J. Chem. Soc. A*, 1508 (1971).

(9) In refluxing benzene,  $(C_5H_5)_2TaH_3$  evolves  $H_2$  to give an intermediate isoelectronic with titanocene: E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, 92, 5235 (1970).

dodecane became optimal while the amount of olefin approached zero. Olefin reduction during the overall reaction is consistent with the separate conversion of 1-decene by the usual titanocene preparation to decane in 76-89% yield. When a dodecanal reduction was carried out starting with  $(C_5H_5)(C_5D_5)TiCl_2$ , highly deuterated decane ( $d_1$ - $d_{16}$ ) was formed (as evidenced by gc and mass spectral data), thereby revealing extensive exchange of titanocene deuterium, presumably with hydrogen of intermediate olefin. Further, when an aliquot removed after 3 hr from a dodecanal reaction was quenched with  $D_2O$ , ca. 50% of the dodecane contained two deuteriums (mass spectral), while remaining alkane and 1-dodecene possessed deuterium at ca. natural abundance levels. However, reactions quenched with  $D_2O$  after 72 hr featured substantially less deuterium incorporation. No deuterium was transferred to hydrocarbon product from benzene- $d_6$  solvent. The foregoing results indicate the formation of intermediate titanium-bound olefin, which can be converted to alkane by  $D_2O$ - $H_2O$  or by hydride from cyclopentadienide ligands. Similar deuterium labeling results were secured with ethyl dodecanoate, thus sug-



gesting that with esters initial reduction to the aldehyde level is followed by steps identical with those involved in reductions starting with aldehydes. In keeping with the suggested scheme, no hydrocarbon was formed from aldehydes and esters which would not be expected to form olefins, including aromatic aldehydes and 1-adamantane carboxylic acid methyl ester. Although the driving force for the conversion of aldehyde to olefin must be formation of the titanium-oxygen bond by a reactive titanocene species, the exact mechanism of deoxygenation has not been established. That epoxide deoxygenation conforms to the pattern is revealed through  $D_2O$  quenching of the 1-decene oxide reaction after 3 hr, whereupon 1-decene, 2-decene, and decane emerged with deuterium levels at or slightly above natural abundance.

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### Structure and Properties of Hydrogen Bonds between the Electronegative Atoms of the Second and Third Rows

Sir:

We report a systematic electronic structure theory study of the hydrogen bond in the hydride dimers involving the atoms N, O, F, P, S, and Cl. Dimerization energies, geometry, dipole moments, and force constants were obtained for 38 dimers, the majority of which have not heretofore been investigated. Complete results are given in Table I and interrelations be-

Table I. Dimerization Energies, Geometry, Dipole Moments, and Force Constants for Hydrogen Bonds Involving Second- and Third-Row Atoms

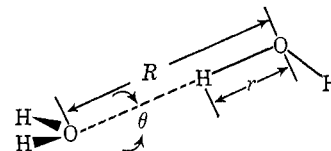
Species	$E_D$ , kcal/mol	$R$ , Å	$\theta$ , deg	$\mu$ , Debyes	$K_{XH}$ , mdyn/Å	$K_{XY}$ , mdyn/Å
H <sub>2</sub> NH...NH <sub>3</sub>	4.13 (4.5 ± 0.4) <sup>a</sup>	3.31	0	4.2	7.18	0.081
H <sub>2</sub> NH...OH <sub>2</sub>	4.07	3.21	55	2.8	7.26	0.120
H <sub>2</sub> NH...FH	3.64	3.26	70	4.9	6.86	0.063
H <sub>2</sub> NH...PH <sub>3</sub>	2.24	4.06	0	3.1	7.33	0.054
H <sub>2</sub> NH...SH <sub>2</sub>	2.16	4.06	80	1.5	7.30	0.020
H <sub>2</sub> NH...ClH	1.35	4.17	80	1.7	6.80	0.010
HOH...NH <sub>3</sub>	8.93	2.95	0	5.0	7.80	0.173
HOH...OH <sub>2</sub>	8.07 (6 ± 3) <sup>b</sup>	2.87 (2.99) <sup>c</sup>	36 (61) <sup>c</sup>	4.4 (2.60) <sup>c</sup>	8.31 (7.04) <sup>d</sup>	0.129
HOH...FH	5.41	2.97	60	3.1	8.21	0.104
HOH...PH <sub>3</sub>	4.02	3.70	0	3.8	8.67	0.090
HOH...SH <sub>2</sub>	3.90	3.69	70	2.4	8.68	0.050
HOH...ClH	2.49	3.72	80	2.2	8.72	0.019
FH...NH <sub>3</sub>	16.3	2.69	0	5.4	8.48	0.520
FH...OH <sub>2</sub>	13.4	2.63	0	5.6	8.89	0.365
FH...FH	7.87 (7.0) <sup>e</sup>	2.72 (2.79) <sup>f</sup>	30 (72) <sup>f</sup>	4.8 (2.99) <sup>f</sup>	9.94	0.193
FH...PH <sub>3</sub>	6.91	3.40	0	4.2	9.01	0.127
FH...SH <sub>2</sub>	5.73	3.41	70	3.9	9.09	0.068
FH...ClH	3.47	3.42	70	3.8	9.22	0.026
H <sub>2</sub> PH...NH <sub>3</sub>	1.20	4.30	0	3.5	3.07	0.026
H <sub>2</sub> PH...OH <sub>2</sub>	1.06	4.16	60	2.6	3.11	0.018
H <sub>2</sub> PH...FH	0.99	4.08	75	1.9	3.12	0.033
H <sub>2</sub> PH...PH <sub>3</sub>	0.80	4.80	0	2.1	3.09	0.026
H <sub>2</sub> PH...SH <sub>2</sub>	0.59	4.75	85	1.4	3.10	0.007
H <sub>2</sub> PH...ClH	0.45	4.81	80	1.7	3.11	0.012
HSH...NH <sub>3</sub>	4.35	3.53	0	4.7	4.15	0.063
HSH...OH <sub>2</sub>	3.72	3.50	20	4.4	4.31	0.058
HSH...FH	2.46	3.67	50	3.2	4.43	0.064
HSH...PH <sub>3</sub>	2.10	4.40	0	3.1	4.38	0.044
HSH...SH <sub>2</sub>	1.79 (1.7 ± 0.3) <sup>g</sup>	4.39	70	2.3	4.35	0.020
HSH...ClH	1.11	4.36	75	2.1	4.42	0.007
ClH...NH <sub>3</sub>	10.9 (15.2 ± 3) <sup>h</sup>	3.14	0	5.6	4.14	0.255
ClH...OH <sub>2</sub>	8.34	3.14	0	5.5	4.57 (3.98) <sup>k</sup>	0.241
ClH...FH	4.58	3.29	45	4.4	4.88	0.090
ClH...PH <sub>3</sub>	4.37	3.98	0	3.9	4.75	0.063
ClH...SH <sub>2</sub>	3.40	4.03	65	3.7	4.81	0.043
ClH...ClH	2.00	4.10	70	3.3	4.91	0.017
H <sub>3</sub> COH...OHCH <sub>3</sub>	7.27 (4.1 ± 0.5) <sup>i</sup>	2.83	0	4.8		0.204
ClH...O(CH <sub>3</sub> ) <sub>2</sub>	8.63 (7.1 ± 0.8) <sup>j</sup>	3.07	0	5.3	4.57	0.202
NH <sub>3</sub>		1.01 <sup>l</sup>		2.28 (1.47) <sup>m</sup>	7.24 (6.5) <sup>m</sup>	
OH <sub>2</sub>		0.957		2.61 (1.85) <sup>m</sup>	8.69 (7.8) <sup>l</sup>	
FH		0.917		2.28 (1.82) <sup>m</sup>	9.25 (9.67) <sup>n</sup>	
PH <sub>3</sub>		1.41		1.05 (0.58) <sup>m</sup>	3.07 (3.1) <sup>n</sup>	
SH <sub>2</sub>		1.32		1.78 (0.97) <sup>m</sup>	4.39 (4.3) <sup>n</sup>	
ClH		1.27		1.86 (1.08) <sup>m</sup>	4.92 (5.15) <sup>n</sup>	
CH <sub>3</sub> OH		0.956		2.4 (1.70) <sup>m</sup>		
O(CH <sub>3</sub> ) <sub>2</sub>		1.41 R(O-C)		2.0 (1.30) <sup>m</sup>		

<sup>a</sup> Experimental values are given in parentheses. Measured value for (NH<sub>3</sub>)<sub>2</sub> from J. E. Lowder, *J. Quant. Spectrosc. Radiat. Transfer*, **10**, 1085 (1970). <sup>b</sup> From J. E. Harries, W. J. Burroughs, and H. A. Gebbie, *ibid.*, **9**, 799 (1969). Another value is 3–5 kcal/mol, see P. Varansi, S. Chow, and S. S. Penner, *ibid.*, **8**, 1537 (1968). <sup>c</sup> T. R. Dyke and J. S. Muentzer, private communication. The dipole moments for (H<sub>2</sub>O)<sub>2</sub> and (HF)<sub>2</sub> have been projected along the heavy atom line to make comparison with the experiments. The unprojected moments are 4.4 and 4.9 D, respectively. <sup>d</sup> A. J. Tursi and E. R. Nixon, *J. Chem. Phys.*, **52**, 1521 (1970). <sup>e</sup> E. U. Frank and F. Meyer, *Z. Elektrochem.*, **63**, 577 (1959). <sup>f</sup> T. R. Dyke, B. J. Howard, and W. Klemperer, *J. Chem. Phys.*, **56**, 2442 (1969). <sup>g</sup> J. E. Lowder, L. A. Kennedy, K. G. P. Sulzman, and S. S. Penner, *J. Quant. Spectrosc. Radiat. Transfer*, **10**, 17 (1970). <sup>h</sup> P. Goldfinger and G. Verhaegen, *J. Chem. Phys.*, **50**, 1467 (1969). <sup>i</sup> A. D. H. Clague, G. Govil, and H. J. Bernstein, *Can. J. Chem.*, **47**, 625 (1969). <sup>j</sup> G. Govil, A. D. H. Clague, and H. J. Bernstein, *J. Chem. Phys.*, **49**, 2821 (1968). <sup>k</sup> B. S. Ault and G. C. Pimentel, *J. Phys. Chem.*, **77**, 57 (1973). <sup>l</sup> For monomers this column is the heavy-atom-hydrogen bond length: W. Gordy and R. L. Cook in "Techniques of Organic Chemistry," Vol. IX, 2nd ed, part 2, A. Weissberger, Ed., Interscience, New York, N. Y., 1970. <sup>m</sup> R. D. Nelson, D. R. Lide, and A. A. Maryott, U.S. Department of Commerce, Nat. Bur. Standards, NSRDS-NBS 10 (1967). <sup>n</sup> E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

tween the dimerization energies are displayed in Figure 1.

The calculations were carried out *ab initio* at the 4-31G s,p basis set level with the GAUSSIAN 70 computer program.<sup>1</sup> Experimental monomer geometries were employed, and the heavy-atom separation,  $R$ , was optimized. This was followed by  $\theta$  and  $r$  optimization. Only linear dimers were considered, and the geometry

definition, illustrated by (H<sub>2</sub>O)<sub>2</sub>, is shown below.



Dimerization energy,  $E_D$ , is defined as the energy difference between the dimer (at equilibrium  $R$  with experimental monomer geometries) and the energy of the separated monomers.

(1) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

As can be seen by comparison with the limited amount of experimental data available, the agreement for dimerization energies, heavy-atom separations, and X-H stretching force constants,  $K_{XH}$ , is moderately good. It appears that simultaneous optimization of both the proton and heavy-atom positions is only necessary for  $\text{ClH} \cdots \text{NH}_3$ , and, when this was carried out, the heavy atoms become 0.1 Å closer together, the proton moves 0.1 Å from its monomer position toward the nitrogen lone pair, and  $E_D$  becomes 12.8 kcal/mol. Dimer dipole moments are overestimated to the same degree traditionally found for separated monomers.

The results reported here parallel those for the second-row dimers found by Kollman and Allen<sup>2</sup> using a Hartree-Fock atomic orbital basis set, and comparison with other earlier work can be found in the review by these authors.<sup>3</sup> The water dimer has been studied more extensively than any other, and, since publication of the review noted above, two important new calculations have been reported. Curtiss and Pople<sup>4</sup> employed the 6-31G\* basis (which includes d polarization functions) and obtained  $E_D = 5.6$  kcal/mol,  $R = 2.97$  Å,  $\theta = 57^\circ$ , and  $K_{OH} = 8.66$  mdyn/Å. Popkie, Kistenmacher, and Clementi<sup>5</sup> used a very large basis set, including s, p, d, and f functions on oxygen and s, p, and d on hydrogens, and they obtained  $E_D = 3.90$  kcal/mol,  $R = 3.0$  Å, and  $\theta = 30^\circ$ . Two interesting and pertinent papers by Sabin<sup>6</sup> on  $(\text{H}_2\text{S})_2$  and Kollman, *et al.*,<sup>7</sup> on  $(\text{HF})_2$ ,  $\text{H}_2\text{OHF}$ ,  $\text{H}_3\text{NHF}$ ,  $\text{HClHF}$ ,  $(\text{HCl})_2$ ,  $\text{HFHCl}$ ,  $\text{H}_2\text{OHCl}$ , and  $\text{H}_3\text{NHCl}$  employ wave functions of higher total energies than 4-31G. The STO-3G basis used by Kollman, *et al.*, yields an erratic ordering of the six monomer dipole moments relative to the experimental values while 4-31G gives the correct order.  $R$  values from STO-3G are also appreciably shorter than with 4-31G. Comparing our 4-31G basis set results with the available experimental data shows that our  $E_D$  values are poorest when oxygen acts as a proton donor and suggests that our  $E_D$  estimates for these systems are approximately 25% too large. Other  $E_D$  estimates may be reliable to  $\pm 15\%$ . Experiment and the most accurate theoretical work on  $(\text{HF})_2$  and  $(\text{H}_2\text{O})_2$  suggest that our  $R$  values are 5% too small. In a similar manner, dipole moments should be multiplied by 0.6 and force constants,  $K_{XH}$ , by 0.85. Some of the  $K_{XH}$  are in error (*e.g.*, some show a blue shift) because we have used experimental rather than theoretically determined monomer geometries.

An analysis of hydrogen bonding using the wave functions for the dimers presented here and a more extended comparison with other work will be reported shortly. During the course of this research we learned that P. Kollman, J. McKelvey, A. Johansson, and S. Rothenberg have been carrying out similar computations.  $E_D$ ,  $R$ , and  $\theta$  values have been compared and we have agreement within 0.1 kcal, 0.05 Å, and  $10^\circ$ . We have enjoyed numerous useful and stimulating conversations with Peter Kollman. We also acknowledge

(2) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **52**, 5085 (1970); *J. Amer. Chem. Soc.*, **92**, 753 (1970).

(3) P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 283 (1972).

(4) L. A. Curtiss and J. A. Pople, to be submitted for publication.

(5) H. Popkie, H. Kistenmacher, and E. Clementi, *J. Chem. Phys.*, **59**, 1325 (1973).

(6) J. R. Sabin, *J. Amer. Chem. Soc.*, **93**, 3613 (1971).

(7) P. A. Kollman, A. Johansson, and S. Rothenberg, *Chem. Phys. Lett.*, **24**, 199 (1974).

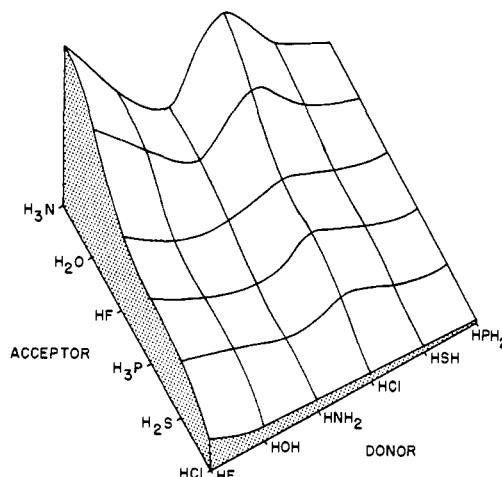


Figure 1. Dimerization energies,  $E_D$ , for the hydrides of the electronegative atoms in the second and third rows.

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### Stereochemistry of Nitrosylmetalloporphyrins. Nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(1-methylimidazole)iron and Nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(4-methylpiperidine)manganese

Sir:

There is much current interest in the structure and bonding of the small molecules, dioxygen, nitric oxide, and carbon monoxide, with metalloporphyrins and in their relationship to the corresponding hemoprotein complexes.<sup>1</sup> We wish to report the structures of two six-coordinate nitrosylmetalloporphyrins, nitrosyltetraphenylporphinato(1-methylimidazole)iron,  $\text{ONFeTPP}(\text{NMeIm})$ , and nitrosyltetraphenylporphinato(4-methylpiperidine)manganese,  $\text{ONMnTPP}(\text{MPip})$ . These compounds represent models of the coordination group in the respective nitrosylmetalloproteins.<sup>1f,1g</sup>

The compounds were prepared by reductive nitrosylation<sup>1a,2</sup> and recrystallized, under an argon-nitric oxide atmosphere, from chloroform solutions containing a large excess of the nitrogen base. The structures of the two molecules have been determined by X-ray diffraction techniques. Both crystallize in the ortho-

(1) (a) W. R. Scheidt and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8281 (1973); (b) J. P. Collman, R. R. Gagne, T. R. Halbert, J.-C. Marchon, and C. A. Reed, *ibid.*, **95**, 7868 (1973); (c) B. B. Wayland and L. W. Olson, *J. Chem. Soc., Chem. Commun.*, 897 (1973); (d) D. V. Stynes and B. R. James, *ibid.*, 325 (1973); (e) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 4087 (1973); (f) J. C. W. Chien, *ibid.*, **91**, 2166 (1969); L. C. Dickinson and J. C. W. Chien, *ibid.*, **93**, 5036 (1971); (g) T. Yonetani, H. Yamamoto, J. E. Erman, J. S. Leigh, Jr., and G. H. Reed, *J. Biol. Chem.*, **247**, 2447 (1972).

(2) (a) D. Gwost and K. G. Caulton, *Inorg. Chem.*, **12**, 2095 (1973). (b) The nitrosyl manganese complex is readily prepared by treatment of a chloroform solution of  $\text{ClMnTPP}$  with nitric oxide in the presence of an excess of 4-methylpiperidine. The complex is easily isolated by the addition of methanol. The general nature of the reaction is being investigated, P. L. Piculo and W. R. Scheidt, to be submitted.