going from 71 to 4°. The most reasonable explanation of the results is a change in conformation of both ribose rings in the dimer.[22,23] Moreover, the lack of any significant $J_{H_{1'}H_{2'}}$ changes in the monomers also suggests that the conformational changes in the dimers are related to the base-stacking interactions. This is strongly supported by the linear correlation[25] between the $H_{1'}$ chemical shifts and the corresponding $J_{H_{1'}H_{2'}}$ coupling constants (see Figure 1). Earlier work[13-15] has shown that the downfield shift of the base ring and $H_{1'}$ proton signals with increasing temperature can be associated with a progressive intramolecular destacking of the base rings in the dimer.

A qualitative picture of the conformational changes can be deduced from a consideration of known ribose structures and the dependence of vicinal couplings upon dihedral angle, ϕ. X-Ray diffraction studies of the crystal structures of purine nucleosides and nucleotides,[26-28] the dinucleoside monophosphate ApU (2'→5'),[29] and a variety of polyribonucleotides[30] have shown that the ribose ring is in a puckered conformation with either the $C_{2'}$ or the $C_{3'}$ atom displaced out of the plane defined by the $C_{1'}$, $C_{4'}$, $O_{1'}$, and $C_{3'}$ (or $C_{2'}$) atoms. In general the out-of-plane atom is in an *endo* position, *i.e.*, located on the same side of the plane as the $C_{5'}$ atom. In only one known case, deoxyadenosine, does the out-of-plane atom ($C_{3'}$) lie in an *exo* position. A rough estimate of the $J_{H_{1'}H_{2'}}$ coupling constants expected for the 2'-*endo* (out-of plane) and 3'-*endo* (out-of-plane) conformations can be made from Karplus' equation for vicinal couplings.[31] Thus, for $C_{2'}$ *endo*, ϕ is approximately 150°[33] and $J_{H_{1'}H_{2'}}$ is estimated to be 6.9 cps, while, for $C_{3'}$ *endo*, $\phi \approx 115°$ and $J_{H_{1'}H_{2'}}$ is estimated to be 1.7 cps. Accordingly at low temperature where the bases are predominantly stacked (<25–30°), the ribose groups of the dimers favor a conformation in which the $C_{3'}$ is in an *endo* orientation, while at elevated temperatures, where the bases are unstacked, the preferred conformation is one in which $C_{2'}$ is *endo*.[34]

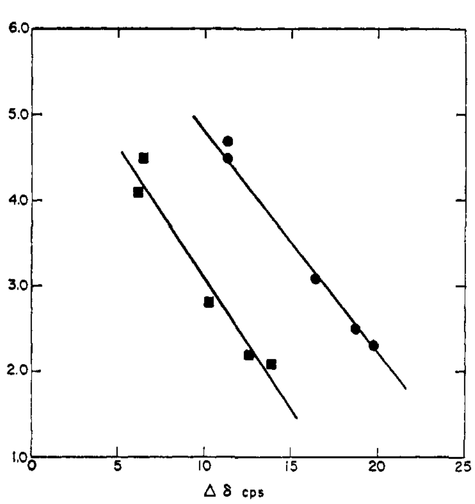

Figure 1. Plot of $J_{H_{1'}H_{2'}}$ *vs.* the respective $H_{1'}$, chemical shifts of the Ap (■) and pA (●) moieties of ApA (the shifts are relative to the values for the corresponding mononucleotides).

The temperature dependence of $J_{H_{1'}H_{2'}}$ for the dimers therefore indicates a conformational change of the ribose group from the $C_{3'}$-*endo* form at low temperatures to a $C_{2'}$-*endo* form at high temperatures. The similarity in magnitude of $J_{H_{1'}H_{2'}}$ in the monomers and dimers at higher temperatures also suggests that the ribose conformations in the unstacked dimers are not significantly different from the monomers.

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[22] It is highly improbable that the J changes are due to any perturbation of electron density at C_1' and C_2' either intramolecularly (*i.e.*, by inductive effects) or by solvent molecules.

[23] Temperature-dependent conformational changes are known to produce significant changes in coupling constants in many saturated ring systems.[24] The absence of coupling constant changes for pA-c-p suggests that conformational changes have been restricted by the 2',3'-cyclic phosphate linkage.

[24] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Inc., New York, N. Y., 1965, p 575.

[25] A linear correlation is also noted between the coupling constants and the chemical shifts of the H_2 (and H_8) protons of the purine bases.

[26] M. Sundaralingam, *J. Am. Chem. Soc.*, 87, 599 (1965).

[27] M. Sundaralingam and L. H. Jensen, *J. Mol. Biol.*, **13**, 930 (1965).

[28] J. Kraut and L. H. Jensen, *Acta Cryst.*, **16**, 930 (1965).

[29] E. Shefter, M. Barlow, R. Sparks, and K. Trueblood, *J. Am. Chem. Soc.*, **86**, 1862 (1964).

[30] D. M. Davies, *Ann. Rev. Biochem.*, **36**, 339 (1967).

[31] The equation is of the form[16] $J_{\text{vicinal}} = A \cos^2 \phi - 0.028$, where $A = 8.5$ for $0° \leq \phi \leq 90°$ and $A = 9.5$ for $90° \leq \phi \leq 180°$. Although the magnitudes of the coupling constants estimated by this equation may be subject to considerable error, the essential form and predicted trends have been confirmed by a number of experimental studies.[20,21,24,32]

[32] R. U. Lemieux, *Can. J. Chem.*, **39**, 116 (1961).

[33] The dihedral angles were estimated from Koltun molecular models.

[34] A C_3' *endo* conformation is supported in the crystalline state by X-ray diffraction studies on AMP-5'[28] and poly A[35] while the $C_{2'}$ *endo* conformation is indicated from nmr studies on a number of purine mononucleosides and nucleotides.[20,21] One can consider the stacked form of the dimer as approximating the structure of the polynucleotide in the solid state.

[35] A. R. Rich, D. R. Davies, F. H. C. Crick, and J. D. Watson, *J. Mol. Biol.*, **3**, 71 (1961).

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Electron Spin Resonance of Nitrogen Dioxide (NO_2) Adsorbed on Zinc Oxide

Sir:

In the course of an investigation of the interaction of oxides of nitrogen with nonstoichiometric surfaces of metallic oxides, the electron spin resonance spectra of NO_2 adsorbed on zinc oxide has been investigated. High-purity ZnO samples supplied by the New Jersey Zinc Co. with surface areas of ~3 m²/g were employed. Prior to treatment with NO_2, samples were outgassed for 2 hr at 500° at 10^{-6} torr. The NO_2 employed was of ultrahigh purity and was supplied by Cryogenic Rare Gas Laboratories Inc., Newark, N. J. Experiments were done with an X-band Varian spectrometer (Model V-4502) provided with a TE_{104} mode dual cavity. A wave meter was used to measure the correct frequency and 1,1-diphenylpicrylhydrazyl (DPPH) was used in the reference cavity as a standard for g measurements.

The esr spectrum of vacuum-outgassed ZnO at −195°, shown in Figure 1A, primarily consists of a signal, at $g \simeq 1.96$ ($\Delta H = 7.6$ G) which is variously assigned to Zn^+ ions,[1,2] oxide ion vacancies,[3] or to conduction electrons.[4] Following treatment with excess

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[1] K. A. Muller and J. Schneider, *Phys. Letters*, **4**, 2288 (1963).

[2] Y. Fujita and J. Turkevich, *Discussions Faraday Soc.*, **41**, 407 (1966).

[3] P. H. Kasai, *Phys. Rev.*, **130**, 989 (1963).

[4] R. J. Kokes, *J. Phys. Chem.*, **66**, 99 (1962).

Table I. Magnitudes of the Principal Values for *g* and *A* for NO_2 Molecule

Nature of NO_2	*g* value			*A* value, Mc sec^{-1}				Anisotropic component			Ref
	g_x	g_y	g_z	A_x	A_y	A_z	A_{iso}	A_x'	A_y'	A_z'	
Adsorbed on ZnO	2.007	1.994	2.003	146.1	132.0	181.1	153.1	−7.0	−21.1	28.0	Present work
In irradiated Na NO_2	2.0057	1.9910	2.0015	138.4	130.9	190.2	153.2	−14.8	−22.3	37.0	7
Adsorbed on MgO	2.005	1.9915	2.002	148.8	136.7	189.0	158.2	−9.4	−21.5	30.8	8

NO_2 (50 torr) at 25°, the spectrum obtained at −195° (Figure 1B) revealed not only a considerable decrease (*ca.* 80%) in the intensity of the signal at $g \simeq 1.96$ but also showed the simultaneous formation of a new sharp (peak-to-peak width = 3 G), symmetric signal at a *g* value of 2.015. Temperature variation of the sample in the cavity showed that the signal decreased in intensity with increasing temperature and was not observed above −130°.

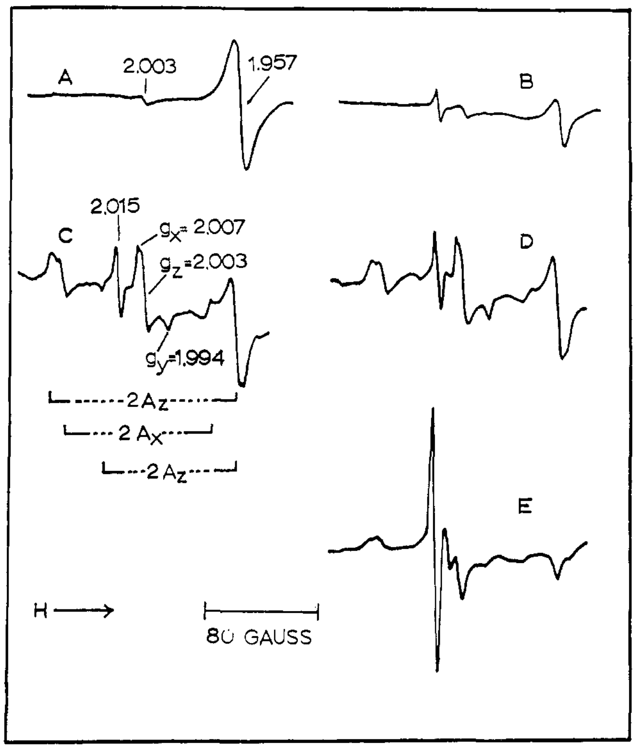

Figure 1. Esr (X band) spectra of nitrogen dioxide adsorbed on ZnO: (A) sample outgassed at 500° for 2 hr at 10^{-6} torr (SL 100, 10 db); (B) exposed at 25° to 50 torr of NO_2 (SL 100, 10 db); (C) excess NO_2 removed by outgassing at 25° for a few minutes (SL 200, 3 db); (D) excess NO_2 removed by outgassing at 25° for a few minutes (SL 500, 15 db); (E) outgassed at 300° for 90 min (SL 200, 10 db). All spectra recorded at −195°.

Outgassing the sample exposed to NO_2 at 25° for a few minutes leads to observation of a different spectrum shown in Figure 1C. The spectrum obviously consists of the singlet at $g = 2.015$ shown in Figure 1B superimposed on a complex pattern. No such pattern was observed under similar conditions on condensation of NO_2 as N_2O_4 in an empty tube placed in the cavity. Also, power variation studies (*e.g.*, Figure 1D) indicate that the complex pattern changes uniformly in intensity which means that the entire spectrum except the signal at $g = 2.015$ is caused by a single species.

A careful study of our complex pattern shown in Figure 1C indicates that the signal should be attributed to rigid NO_2 molecules adsorbed on ZnO. The complexity of the observed spectrum apparently arises from the fact that both *g* and hyperfine anisotropic contributions are present. Thus, when each of the g_x, g_y, and g_z components are split into three lines due to interaction with an ^{14}N nucleus ($I = 1$), one normally expects the hyperfine components in each set to be of equal intensity. However, for powder samples it is known[5] that the lines corresponding to $m_I = \pm 1$ are broadened compared to the line with $m_I = 0$. The principal *g* and *A* values obtained from an analysis of the complex pattern are shown in Table I. The assignment of values for g_x, g_y, and g_z are such that $g_x > 2.003$, $g_y < 2.003$, and $g_z = 2.003$ in accordance with the work on the isoelectronic CO_2^- molecule.[6] Also included in Table I for comparison are the corresponding values reported for (a) NO_2 in irradiated $NaNO_2$[7] and (b) NO_2 adsorbed on high area MgO.[8] The obvious similarity in these values support our assignment of the complex spectrum to adsorbed NO_2 molecules.

On vacuum outgassing the sample, exposed to NO_2 vapors at 25°, at progressively higher temperatures, the complex signal is observed to decrease in intensity. Figure 1E is the spectrum obtained following outgassing of the sample at 300° for 90 min. The spectrum shows clearly the presence of two signals at $g = 2.003$ and $g = 2.007$, respectively, previously seen poorly resolved (Figure 1C). Additional outgassing at 500° for 30 min does not bring about a complete removal of the signal. These experiments establish clearly that the species responsible for the signal (identified as NO_2) is strongly adsorbed.

Since no electron transfer is involved in the adsorption of NO_2 on ZnO, the adsorption itself is independent of Zn^+ ions or oxygen ion vacancies in the sample. Thus, the appearance of the NO_2 spectrum is independent of the presence or absence of the signal at $g \simeq 1.96$. In fact, the esr spectrum of NO_2 is as easily obtained on ZnO vacuum outgassed at 500° as on a sample previously heated in oxygen at 500° to restore the stoichiometry.

The origin of the sharp, symmetric signal at $g = 2.015$ is less clear. This signal is most intense on samples outgassed at 300° after exposure to NO_2 at 25° (Figure 1E) and decreases in intensity following outgassing at higher temperatures. A similar signal was also obtained in our studies on treatment of vacuum outgassed ZnO at 25° with chlorine.

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(5) A. J. Tench and R. L. Nelson, *Trans. Faraday Soc.*, **64**, 2254 (1967).

(6) D. W. Ovenall and D. H. Whiffen, *Mol. Phys.*, **4**, 135 (1961).

(7) H. Zeldes and R. Livingston, *J. Chem. Phys.*, **35**, 563 (1961).

(8) J. H. Lunsford, presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract H 75.

In general no sharp, symmetric signal at $g = 2.015$, such as observed in the present study, has been reported in the literature except for the work of Terenin, *et al.*[9] These authors noticed the formation of such a signal ($\Delta H = 3$ G; $g = 2.018$) in the esr spectrum by uv irradiation of a ZnO sample at 77°K. While the species responsible for the signal was not identified, it was suggested later[10] that the singlet was caused by chemisorbed oxygen atoms.

The observation made in the present study that chlorine treatment of the sample produces the sharp signal at $g = 2.015$ indicates that the signal is not caused by chemisorbed oxygen atoms. While a positive identification of this signal cannot be made at the present time, the results so far obtained suggest the presence of shallow levels on ZnO which give rise to the signal following loss of an electron to the interacting gas at the surface.

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(9) E. V. Baranov, V. E. Kholmogorov, and A. N. Terenin, *Dokl. Akad. Nauk SSSR*, **146**, 125 (1962).

(10) V. Ya. Vol'fson and L. N. Garyuk, *Russ. Chem. Rev.*, **34**, 701 (1965).

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The Preparation and Crystal Structure of $(CH_3)_5Al_2N(C_6H_5)_2$, μ-Diphenylamino-μ-methyl-tetramethyldialuminum[1]

Sir:

In reactions of trialkyls or triaryls of group III metals such as Al, Ga, and In, with secondary aliphatic or aromatic amines, phosphines, and arsines, the resulting product is generally a dimeric or trimeric species, $[R_2M\cdot XR_2']_{2,3}$ (M = Ga, Al, In; X = N, P, As; R, R′ = alkyl, aryl).[2,3] These dimers or trimers consist of metal atoms bridged by amino, phosphino, or arsino groups which, as three electron donors, form normal Lewis electron-pair bonds. This is in contrast to the trimethylaluminum dimer in which the methyl groups occupy bridging positions and form three-center electron-deficient bonds.[4]

We wish to report here the preparation and crystal structure of a compound which simultaneously displays both types of bonding, $(CH_3)_5Al_2N(C_6H_5)_2$. This complex was prepared in our laboratory by the vacuum distillation of 20 mmoles of trimethylaluminum into a cold tube (−196°) containing 10 mmoles of diphenylamine. The reaction mixture, which was under a positive pressure of N_2, was allowed to warm slowly to room temperature and then heated to 100°. Methane was given off during the course of reaction. Excess trimethylaluminum was pumped off and the product was sublimed as clear colorless rectangular rods at 10^{-3} mm and 75°.

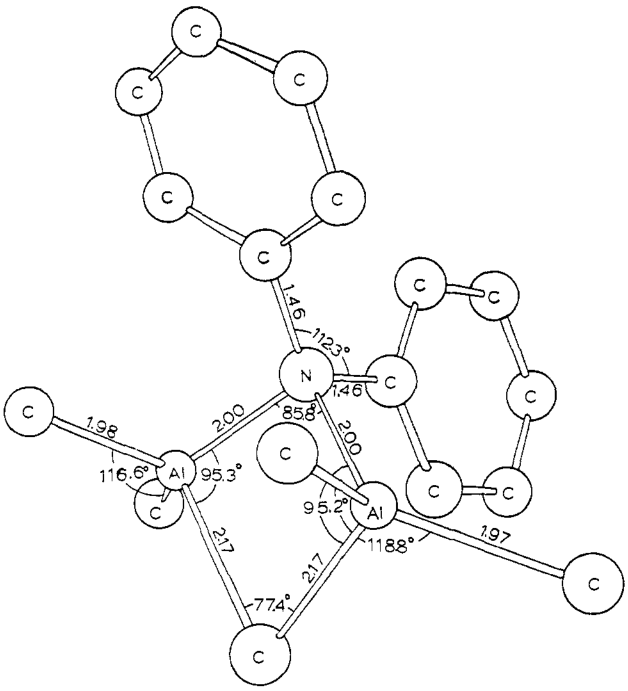

Figure 1. The molecular configuration of $(CH_3)_5Al_2N(C_6H_5)_2$.

Trimethylaluminum has been shown to crystallize as dimers with electron-deficient bridge angles (Al–C–Al) of 74.7°.[4] The X-ray structural analysis of $(CH_3)_5Al_2N(C_6H_5)_2$ shows that the crystal consists of dimeric molecules resembling those found in $[Al(CH_3)_3]_2$ but with one bridging methyl group removed and a diphenylamino group substituted in its place (Figure 1). The geometry around each Al atom is distorted from tetrahedral symmetry with exterior C–Al–C angles of 118.8 and 116.6° and interior C–Al–N angles of 95.2 and 95.3°. The Al–N–Al and Al–C–Al bridging angles are 85.8 and 77.4°, respectively. Comparison of the Al–C–Al bridging angle in this compound with $[Al(CH_3)_3]_2$ shows that this angle is only slightly larger (77.4 *vs.* 74.7°) while the Al–N–Al angle agrees favorably with other systems of this type (see below).[5,6] The average bond lengths (Al–N, 2.00 Å; Al–C (bridge), 2.18 Å; Al–C (terminal), 1.98 Å) also agree well with Pauling's sum of covalent radii[7] as well as with previous observations of bond lengths in similar systems.[4,5,8]

This work represents the first description in the solid state of a mixed electron-deficient–nonelectron-deficient bridging situation for the representative elements. Although mixed bridging systems have been previously proposed to explain proton magnetic resonance data for mixtures of $[(CH_3)_2AlN(C_6H_5)_2]_2$,[9] $[Al(C_6H_5)_3]_2$,[10] and $[(CH_3C_6H_5)_3Al]_2$[10] with $[Al(CH_3)_3]_2$, no solids were characterized. Low-temperature proton magnetic resonance studies in our laboratory have shown that $(CH_3)_5Al_2N(C_6H_5)_2$ dissolved in toluene

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[1] This research was supported by the National Science Foundation and by the Advanced Research Project Agency.

[2] G. E. Coates and J. Graham, *J. Chem. Soc.*, 233 (1967).

[3] N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

[4] R. G. Vranka and E. L. Amma, *ibid.*, **89**, 3121 (1967).

[5] V. R. Magnuson and G. D. Stucky, unpublished results.

[6] J. L. Atwood and G. D. Stucky, *Chem. Commun.*, 1169 (1967).

[7] L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

[8] J. L. Atwood and G. D. Stucky, *J. Am. Chem. Soc.*, **89**, 5362 (1967).

[9] M. Kawai, T. Ogawa, and K. Hirota, *Bull. Chem. Soc. Japan*, **37**, 1302 (1964).

[10] E. A. Jeffery, T. Mole, and J. K. Saunders, *Australian J. Chem.*, **21**, 137 (1968).