some average distances and angles. There is no crystallographically imposed molecular symmetry, but there is idealized $C_s(m)$ symmetry, the mirror plane being vertical through Al and H (Ti–H–Ti). Each titanium atom is bonded to two bridging hydrides and h^5 bonded to cyclopentadienide and fulvalenide ligands. Individual C_5 rings are planar (maximum deviation 0.01 Å). The Ti–C distances are 2.353 (4) for C_5H_5 and 2.33–2.39 Å for $C_{10}H_8$; C–C distances are normal. Relative to the TiAlTi plane, two hydride hydrogens (Ti–H–Al) are 0.14 Å below the plane and the third (Ti–H–Ti) is 0.43 Å above the plane (Figure 1b). The angle between C_5 rings on the same Ti atom is 43.2°.

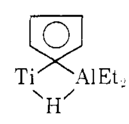
The structure of **3** is shown in Figure 2 along with some distances and angles. The molecule has space group imposed $C_2(2)$ symmetry; the twofold axis is the view direction of Figure 2, with half of the dimer being crystallographically unique. In addition to a Ti–Ti bond, each titanium is h^5 bonded to a bridging C_5H_4, h^1 to the other bridging C_5H_4, and h^5 to half of the $C_{10}H_8$ fulvalenide ligand. Both Ti atoms and C_5H_4 groups are bridged by hydridodiethylaluminum ligands. All individual C_5 rings are planar (maximum deviation 0.02 Å), but the combined fulvalene is not planar (maximum deviation 0.25 Å). The angle between the C_5 planes on the same Ti atom is 45.9°.

The important question arises regarding the presence of Ti–Ti bonds in these compounds. The Ti–Ti distance alone is not a good bond criterion,[7] especially in these systems where the bridging constraints are substantial. The combined data of disposition of valence orbitals, Ti–Ti distance of 2.910 Å, and diamagnetism support a Ti–Ti single bond in **3**. We feel the stereochemistry and 3.374 Å Ti–Ti distance indicates the absence of a regular Ti–Ti bond in **2**. According to the usual electron counting schemes (which are not totally unambiguous here), we might then expect **2** to be paramagnetic; however, the diamagnetism of the compound (Evans method, 30°) could result from superexchange through the bridging hydride hyrogen which is in a good position to participate in Ti atom spin coupling.[8]

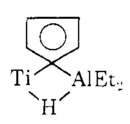
The localized $TiC_5H_4AlEt_2$ geometries of **1** and **3** are closely related. This confirms our earlier prediction of the hydride location in **1**.[1] In addition to the h^5 bonding to Ti, the C_5H_4 group in these compounds is part of a three-center two-electron bond system involving Ti, C, and Al, similar to the situation of C_6H_5 in $(Me_2AlC_6H_5)_2$[9] and $[(C_6H_5)_3Al]_2$.[10,11]

The fulvalenide geometry is quite flexible. The dihedral angle between C_5H_4–C_5H_4 rings varies from 12.5° in **2** (Ti–Ti distance 3.374 Å) to 25.8° in **3** (Ti–Ti distance 2.910 Å), partially in response to the change in metal–metal separation.

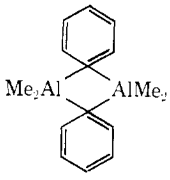
A great deal of speculation has appeared in the literature on the structure of "titanocene."[12] Our structure for $[(C_5H_5)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)$ (**2**) is closely related to a fulvalenide-bridged structure for "titanocene" proposed by Brintzinger and Bercaw.[4] Removal of $HAlEt_2$ from **2**, followed by movement of the remaining hydride to bridge the titanium atoms, would produce $[(C_5H_5)TiH]_2(C_{10}H_8)$ with their proposed structure. We find that hydrolysis of **2** with 1 equiv of water produces "titanocene"[13] in 70% yield after recrystallization. Although the structure of **2** and its facile conversion to "titanocene" do not unambiguously determine the "titanocene" structure, these data support the fulvalenide and hydride bridged structure proposed by Brintzinger and Bercaw.



3



1



$Al–C(C_5H_4)$, 2.06 Å	$Al–C(C_5H_4)$, 2.11 Å[2]	$Al–C(C_6H_5)$, 2.14 Å
Al–Ti, 2.82 Å	Al–Ti, 2.79 Å	Al–Al, 2.69 Å
$Al–C(C_5H_4)–Ti$, 77°	$Al–C(C_5H_4)–Ti$, 77°	$Al–C(C_6H_5)–Al$, 78°

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Effect of Electronic Excitation on Intermolecular Force Constants of Bromine Molecules

Sir:

Observed effects of molecular electronic excitation on intermolecular forces should offer new tests of theories of electronic structure. Changes in polarizabilities $\Delta\alpha = \alpha^* - \alpha$ have been reported for molecules in condensed phases.[1,2] Here, we report the first related results for a molecular vapor; pressure broadening and shift of rotational lines in the electronic absorption spectrum of the Br_2 molecule have been measured and used to calculate changes in Lennard-Jones force constants $\Delta C_6 = C_6^* - C_6$ and $\Delta C_{12} = C_{12}^* - C_{12}$. The change of only 6% inferred for $\Delta\alpha$ contrasts with $\Delta\alpha$ values found for other molecules in condensed phases.

Line shapes of the $B^3\Pi_{0^-_u} \leftarrow X^1\Sigma^+_g$ transition of bromine were studied by means of a Fabry–Perot interferometer spectrometer. Since publication of earlier work with the instrument,[3] a Michelson interferometer has been incorporated for calibration of spectra. Absorption line widths and shifts were measured for lines near a krypton emission secondary standard at 5570.2895 Å and at Br_2 pressures between 0.6 and 132 Torr. The results in Table I exhibit no dependence on quantum numbers. Assuming full-width at half-maximum and position to vary linearly with pressure, we therefore

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Table I. Effect of Pressure on the Position of a ^{81}Br–^{81}Br Line and on the Widths of Some ^{79}Br–^{81}Br Lines (cm^{-1})

Pressure (Torr)[a]	Full-width at half-maximum (cm^{-1})[b]					Position (cm^{-1})[c]
	19-1 band			20-1 band		19-1 band
	R(35)	R(37)	P(39)	R(62)	R(63)	R(31)
0.60	0.028 (4)	0.029 (4)	0.033 (3)	0.031 (4)	0.031 (1)	17,947.921
2.83	0.029 (3)	0.030 (8)	0.034 (3)	0.031 (3)	0.033 (3)	7.913
5.61	0.030 (3)	0.029 (7)	0.035 (3)	0.029 (3)	0.032 (6)	7.915
36.1	0.031 (2)	0.034 (5)	0.037 (3)	0.036 (2)	0.035 (5)	7.914
132	0.054 (2)	0.052 (6)	0.051 (3)	0.051 (2)	0.051 (6)	7.913

[a] At the temperature of 296°K, the *vapor* pressure of bromine was about 181 Torr. [b] Band assignments are in the form $v^* - v$, and line assignments are in the form $R(J)$ or $P(J)$. Each entry is an average of measurements of the number of recordings which appears in the respective parentheses. Lines were chosen because they are not seriously overlapped by their nearest neighbors at any of the pressures; in addition, their quantum numbers are known. The lines are symmetric. [c] The line was chosen because it is very close to the ^{84}Kr secondary standard at 5570.2895 Å (ν_{vac} = 17947.434 cm^{-1}). Measurements of three or more recordings of each of two Fabry–Perot orders were averaged for each entry.

have plotted all of the data, and we find the slopes of the lines to be +0.133 cm^{-1}/atm and −0.03 cm^{-1}/atm, respectively. The uncertainty in the latter is about 30%. The value 0.133 cm^{-1}/atm for broadening may be refined by plotting the Lorentzian contribution to the width rather than the observed width. This correction increases the result by about 20%, which is within the estimate of error.

Earlier measurements of broadening and shift of emission lines of *atoms* have been made. In those cases, successful interpretation[4,5] has been based on the so-called impact approximation (always valid for half-widths at pressures as low as those of Table I) and on the Lennard-Jones potential energy form

$$V = C_{12}r^{-12} - C_6r^{-6}$$

in which r is the interatomic distance. Since broadening of Br$_2$ lines does not show dependence on rotational quantum J, the existing theory has been applied here, with

$$V^*(\mathrm{Br_2}^*:\mathrm{Br_2}) - V(\mathrm{Br_2}:\mathrm{Br_2}) = \Delta C_{12}r^{-12} - \Delta C_6r^{-6}$$

in which r is now the intermolecular distance and each of the empirical force constants ΔC_{12} and ΔC_6 is the difference between an excited-state value (*) and a ground-state value. Applying the analysis of Hindmarsh, *et al.*,[5] we find $|\Delta C_{12}| = 3000 \times 10^{-104}$ erg cm^{12} and $|\Delta C_6| = 80 \times 10^{-60}$ erg cm^6. It is useful to compare these differences with the values of C_{12} and C_6 for two ground-state Br$_2$ molecules; from the corresponding-states correlation of Tee, *et al.*,[6] we estimate 640 × 10^{-104} erg cm^{12} and 1300 × 10^{-60} erg cm^6, respectively. Thus, the change in C$_6$ is ~6%.

In rough approximation,[7] ΔC_6 is proportional to $\Delta\alpha$; evidently the ground-state polarizability of Br$_2$ (6.4 × 10^{-24} cm^3/molecule) also is changed by only about 6% in this transition. For comparison with a typical valence-shell promotion, we mention the 2600 Å absorption of C$_6$H$_6$, in solid solution, for which effects of high electric fields indicate an increase of polarizability of more than 20%.[2]

On account of the rather small effects found for bromine, more extensive measurements on the similar electronic transition of chlorine have been started. Details of work on both molecules will be published elsewhere. If they are feasible, high-field studies of the Br$_2$ and Cl$_2$ bands would be of great interest.

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Polarized Electronic Spectra of Tetracyanonickelate(II) at 5°K

Sir:

Ten years have passed since we proposed[1] an interpretation of the aqueous solution electronic absorption spectrum of the square planar (D_{4h}) complex ion, Ni(CN)$_4$$^{2-}$. Our suggestion that the intense, near-ultraviolet bands be assigned as transitions from occupied d orbitals to the a$_{2u}$ (4p$_z$,π*CN) virtual orbital in this low-spin d^8 (^{1}A$_{1g}$ ground state) complex has been largely confirmed by both magnetic circular dichroism (MCD) spectral experiments[2,3] and recent *ab initio* SCF–LCAO–MO calculations.[4] However, there remains a need for absorption band polarization data on optically dilute single crystals, to provide a firm basis for detailed assignments of both the ligand field (LF) and the charge transfer (CT) bands. We have found that suitable crystals can be readily obtained using tetra-*n*-butylammonium as the cation. Here we report the principal results and conclusions of our investigation of the band polarizations of [(n-C$_4$H$_9$)$_4$N]$_2$[Ni(CN)$_4$] at liquid helium temperature.

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