(5), 40% of recovered 3α-cholestanyl acetate, and 19% of polar impurities. Increasing the amount of $PhICl_2$ used to 2.5 equiv afforded 54% of Δ^{16}-3α-cholestenol, mp 119-120°, 7% 3α-cholestanol and 39% of polar impurities.[9,10]

In order to obtain 17-keto steroids, a procedure was needed to convert the Δ^{16} steroids into their $\Delta^{17(20)}$ isomers. This was accomplished by treatment of **5** with *N*-phenyltriazolinedione in methylene chloride (25°, 24 hr) to provide the ene adduct **6** in 65% yield. The stereochemistry of the double bond would result from α attack on the steroid and intramolecular hydrogen transfer. Saponification of **6** followed by reduction with lithium in ethylamine[11] gave *Z*-$\Delta^{17(20)}$-3α-cholestenol (**7**),[12] mp 133-135°, in 74% yield. Acetylation of **7** followed by ozonolysis (ethyl acetate, −20°) afforded androsterone acetate (**8**) in 78% yield,[15] completing a rational conversion of 3β-cholestanol to androsterone acetate. The remote oxidation procedure described may prove useful in converting abundant steroids into the valuable steroidal hormones.

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(10) An alternative approach to 17 functionalization is based on inserting two methylenes into *p*-iodophenylacetic acid to extend it from C-14 to C-17. Chlorination of 3α-cholestanyl 4-(*p*-iodophenyl)butyrate in carbon tetrachloride gave 17% of Δ^{16}-3α-cholestenyl acetate, 19% of Δ^{14}-3α-cholestenyl acetate, and 16% polar impurities. Similar chlorination of the 3-(*p*-iodophenyl)propionate of 5-(*p*-iodophenyl)valerate gave less than 10% of steroidal olefins. If the methylene chain is in the lowest energy extended conformation, the iodophenyl is pointed toward the steroid with an odd number of methylenes and away from the steroid with an even number of methylenes.

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(12) The NMR signal of the 21-CH_3 of **7** occurs at 93 Hz. In the *E* isomer the corresponding absorption occurs at 101 Hz.[13] This dependence of the chemical shift of the methyl group has been previously observed in $\Delta^{17(20)}$ pregnenes.[14]

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Nuclear Magnetic Resonance of Rare Spins. Determination of ^{15}N Parameters from Proton Fourier Transform Nuclear Magnetic Resonance by Elimination of Signals Due to Abundant Isotope

Sir:

Previously we have proposed[1] a method which leads to the abundant isotope signals elimination by Fourier transform NMR (we shall call this method AISEFT). At this time, it was applied to the measurement of ^{13}C–^{1}H couplings. We wish to describe here an extension of this procedure to the determination of ^{15}N parameters. It consists in collecting a first proton interferogram while irradiating ^{15}N transitions and a second one without irradiation. These two data collections are then subtracted, and this sequence is repeated until a suitable S/N ratio is obtained. In this way strong resonances due to molecules containing ^{14}N would in principle disappear and only ^{15}N satellites together with these satellites decoupled from ^{15}N would remain, these latter signals being shifted in phase by an angle of 180°. This procedure is an adaptation to Fourier transform of a method applied by Freeman[2] to CW NMR.

In principle, this method should yield all nitrogen parameters. Unfortunately, due to small instrumental instabilities, the strong peaks do not entirely disappear. This prevents the measurements of small couplings, except when resonances due to molecules containing ^{14}N are broad. This opportunity occurs for formamide (Figure 1). In this case, it has been possible to detect all the couplings between protons and ^{15}N, ^{15}N being in natural abundance: J_{14} = 88.3 Hz, J_{24} = 90.7 Hz, J_{34} = 14.6 Hz. In fact it is always possible to observe splittings larger or equal to 5 Hz, but for the other molecules under investigation (always with ^{15}N in natural abundance), we could only measure the one bond coupling $^{1}J_{NH}$, the other couplings being too small. (A typical AISEFT is shown in Figure 2.) Results are gathered in Table

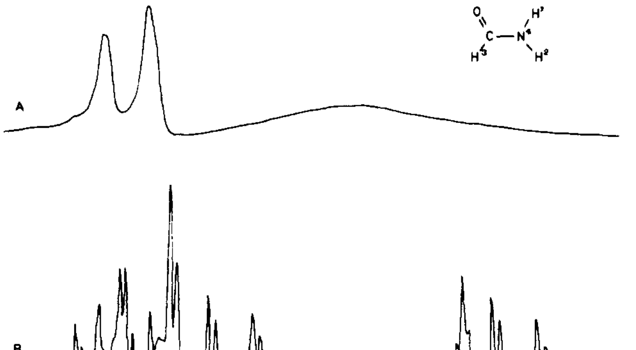

Figure 1. (A) Normal 90-MHz proton spectrum of formamide. (B) AISEFT spectrum. Lines down arising from ^{15}N satellites decoupled of ^{15}N. (C) Theoretical spectrum of $HCO^{15}NH_2$. All spectra were recorded with a Bruker HX 90 spectrometer interfaced with a Nicolet 1080 computer.

Table I

Compound	Solvent	$^1J_{^{15}NH}$ (Hz)
$CH_3CONHCH_3$	Pure	93.0
$CH_3CH_2CONHCH_3$	Pure	92.9
$(CH_3)_2CHCONHCH_3$	Pure	92.7
$(CH_3)_3CCONHCH_3$	CCl_4	92.3
$CH_3CONHCH_2COOCH_3$	Acetone	93.5
$CH_3CONHCH(C_2H_5)COOCH_3$	Acetone	92.6
$CH_3CONHCH(i\text{-}Pr)COOCH_3$	Acetone	92.9

Figure 2. AISEFT spectrum of *N*-methylacetamide (^{15}N being in natural abundance) with ^{15}N satellites corresponding to $^1J_{NH}$. Note the smallness of the residual peak corresponding to molecules containing ^{14}N.

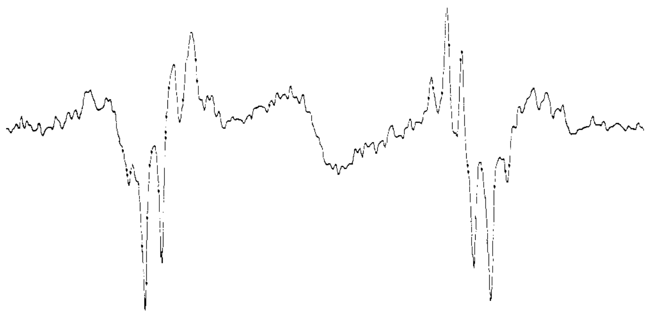

Figure 3. AISEFT spectrum of *N*-methylacetamide with irradiation frequency shifted from ^{15}N resonance. Lines down correspond to the normal undecoupled satellites. The other lines are due to incomplete decoupling and, according to the theory,[6] they appear on each side of the undecoupled peaks.

I. One notices that $^1J_{NH}$ is almost independent on the substitution, (ca. 92–93 Hz) provided that the respective position of N—H and C=O is the same. All these molecules are indeed in the trans conformation.[3,4] (The cis isomer of *N*-methylformamide is in too weak a proportion to enable the determination of the corresponding coupling.) Formamide, however, presents obviously the two arrangements and the cis coupling is seen to be smaller than the trans coupling. This is in agreement with other results obtained from ^{15}N enriched molecules.[4,5]

Another interesting feature of this method lies in the possibility to determine the nitrogen resonance frequency. A small shift of the ^{15}N frequency actually results in the appearance of an off-resonance satellite spectrum together with the normal satellite spectrum. A typical result is shown in Figure 3 for *N*-methylacetamide. It is possible to relate the observed splittings of the off-resonance spectrum to the difference between the irradiation frequency and the true ^{15}N resonance frequency.[6] Consequently two experiments carried out at two different frequencies are sufficient to obtain the ^{15}N chemical shift. For *N*-methylacetamide, we have found 80.881, 284 MHz relative to TMS resonance (the TMS resonance frequency is 90.001, 537 MHz).

In conclusion, two distinct advantages of these experiments have to be pointed out. In one hand, ^{15}N parameters are obtained with proton sensitivity (for a neat liquid in a 5-mm sample, 200 scans are sufficient to observe ^{15}N satellites). On the other hand, the elimination of strong lines arising from molecules containing ^{14}N authorizes a great number of scans without saturating the computer memories.

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A Molecular Orbital Study of the Electronic Structure and Spectrum of Rectangular (D_{2h}) Cyclobutadiene

Sir:

Cyclobutadiene (**1**) was first generated as a transient intermediate by Pettit and coworkers[1] in 1965; subsequently they went on to show that the room temperature chemistry of **1**[2] and its vicinal diphenyl derivatives[3] are characteristic of highly reactive singlet dienes.[4] More recently,[6] however, ir studies of low temperature matrix isolated cyclobutadiene, have been interpreted in terms of a square (D_{4h}) structure for **1**. This result is in apparent contradiction to the earlier work (*vide postea*), and for this reason we have employed the semiempirical MINDO/3 method[7] and *ab initio* molecular orbital theory at the 4-31G level[8] together with the equations of motion (EOM) method[9,10] in the hope of throwing further light on the nature of **1**.

In the simple Huckel MO (HMO) picture of square cyclobutadiene (see Figure 1a), two π-electrons occupy a bonding orbital (π_1) while the remaining two π-electrons are placed in doubly degenerate nonbonding molecular orbitals (π_2, π_3). On distortion of the carbon framework to a rectangular geometry, the degeneracy of π_2 and π_3 is lifted and a closed shell ground state results (Figure 1b).

The electronic states which arise from the open shell electronic configuration of D_{4h} cyclobutadiene are not well described by single determinant molecular orbital theory and, in general, at least two determinants are required to give wave functions of the proper spin and spatial symmetry in such cases.[11a] For this reason we report only our calculations for the rectangular (D_{2h}) geometry at this time; complete results will be presented elsewhere when we have completed our search of the potential hypersurface. However, it is worth noting that the ^1A_g state (Figure 1b) of rectangular cyclobutadiene is the lowest point which we have so far located on the potential hypersurface, (using the MINDO/3 and EOM methods) and lies lower in energy than the square triplet (Figure 1a) when calculated with the MINDO/3 (half-electron scheme) or *ab initio* 4-31G (RHF and UHF) methods.[11b]

The calculated equilibrium geometries for D_{2h} cyclobutadiene are given in Table I. As expected, a large alternation of bond lengths is found, in agreement with previous theoretical treatments[12] and with X-ray structural analyses of sterically crowded cyclobutadienes.[13] The term antiaromatic[14,15] is clearly justified as the degree of bond alternation