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Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)

CRYSTAL AND DENSITY FUNCTIONAL THEORY MOLECULAR STRUCTURE OF THE CYCLOBUTANONE RESULTED FROM THE CYCLOADDITION OF t-BUTYLCYANOKETENE (MOORE'S KETENE) WITH INDENE

Luminitza PÂRVULESCU,*[a] Anca MARTON,[a] Constantin DRĂGHICI,[b] Richard A. VARGA[c] and Mircea D. GHEORGHIU*[d]

[a] Faculty of Applied Chemistry and Materials Science, "Politehnica" University of Bucharest, Splaiul Independentei 313, 060042 Bucharest, Roumania
[b] "C. D. Nenitzescu" Institute of Organic Chemistry, Roumanian Academy, Splaiul Independentei 202B, 060023 Bucharest, Roumania
[c] Chemistry Department, Babes-Bolyai University, Cluj-Napoca, Arany Janos Str. no. 11, RO-400028 Cluj, Roumania
[d] Department of Chemistry, Massachusetts Institute of Technology 4-449, Massachusetts Av. 77, Cambridge, MA 02139, USA

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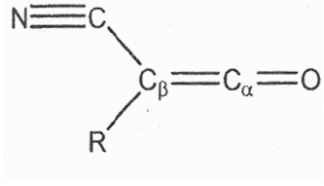
The cycloaddition of *t*-butylcyanoketene (Moore ketene) with indene is regio- and stereospecific. X-ray diffraction study of the only resulted cyclobutanone **3a** illustrates that the CO group is in the vicinity of the indenic CH_2 group and the *t*-butyl is *cis* (or *endo*) to the indene substructure. Steric congestion among the *t*-Bu and aromatic ring is partly alleviated by the lengthening of the C-C bond bearing those groups to 1.602 Å. The cyclobutanone folding angle along the transanular line not comprising the carbonyl is of 2.04 degrees. B3LYP/6-31g(d) calculations satisfactorily predict the experimental geometry. Calculations have also provided information concerning that cyclobutanone **3a** is thermodynamically the least stable among the four regio- and stereoisomers. The energies of activation for TBCK cycloaddition with indene, to yield cyclobutanone **3a** is forecasted to be of $\Delta G^{\ddagger} = 22.0$ kcal/mol, while to formation of the more stable thermodynamically cyclobutanone **4** is of $\Delta G^{\ddagger} = 36.7$ kcal/mol. The predicted GIAO chemical shifts for the ^1H and ^{13}C NMR are instrumental in the signals assignment.

INTRODUCTION

In the year 2005 the chemical community celebrated the centennial[1a,b] since Staudinger[1c,d] discovered the reactive intermediate of ketenes. In recognition, a special symposium has been dedicated to this event during the International Chemical Congress of the Pacific Basin Societies (Pacifichem 2005, Honolulu, Hawaii, December, 15-20, 2005).

The reactivity of ketene can be modulated by substituents that encompass a large window of electronic demands.[1e,f] In particular, the cyano group is enhancing the electrophilicity of atom C_α (Natural Bond Orbital charge is 0.765 e) which is the spearhead of the cycloaddition, compared with the same carbon atom from the parent ketene (Natural Bond Orbital charge is 0.693 e).[1f]

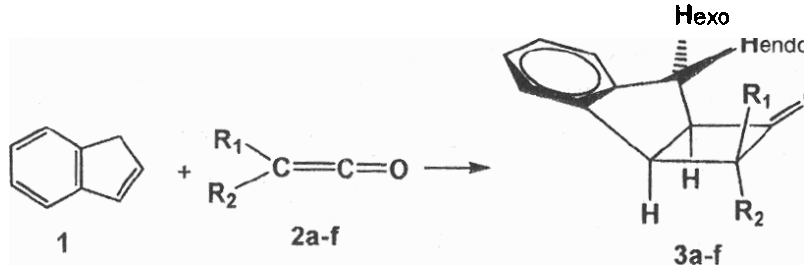


* Corresponding authors: mircea@mit.edu; lr_parvulescu@chim.upb.ro

Among the known cyanoketenes (R=H,[2a] Ph,[2b] alkyl,[2c] CN,[2d] Cl[2e], 2-Pyridinyl[2f]) so far, only *t*-butylcyanoketene (TBCK or Moore's ketene) has emerged with a proven record of attractiveness. Its inherent asymmetry corroborated with the stereochemical outcome of the cyclobutanones resulted from cycloadditions across C=C double bond (appropriately substituted with bulky or rigid group(s)), are very powerful assets to learn about the regio- and stereochemistry preference of TBCK. For example, both our previous works[3,4] and that of Hussain *et al.*[5] regarding single-crystal X-ray crystal structure of cyclobutanones resulted from the cycloaddition of TBCK with vinyl derivatives R-CH=CH_2 (R=Ph,[3] 1-napthyl,[3] -$(CH_2)_3OSi(CH_3)_2{}^tBu$)[5] and to bicyclo[2.2.1]heptene derivatives[4] revealed that TBCK adds across the C=C bond of the ketenophile such as that the *t*-butyl group has *cis* configuration in respect to R or to the CH_2 group from the norbornene small bridge.

Indene is an ideal substrate to test the regio- and the stereochemistry of unsymmetrical substituted ketene cycloaddition. Regio- and stereochemical features of the cyclobutanone resulted from TBCK + indene cycloaddition, based upon NMR analysis, have been discussed in our previous work.[6] Two other known example of asymmetric ketene cycloaddition to indene are the PhS-C(CH_3)=C=O[7a] and PhS-CH=C=O,[7b] respectively. All these cyclobutanones have identical regio- and stereochemistry, namely the C=O vicinal to the indene CH_2 group and the bulky group, *t*-Bu or ArS-, in the *endo* configuration. Cycloaddition of symmetrical substituted ketenes, R_2C=C=O (R=Cl,[8] CH_3,[9] C_6H_5[10]), follows the same regiochemistry, namely, C=O group in the vicinity of the CH_2 group.

In this contribution we present our X-ray diffraction results that substantiate the structure of the cyclobutanone **3a** resulted from cycloaddition of TBCK with indene that had previously been inferred from NMR data.[6] Also, the computational modeling of the regio- and stereoisomers provides insights regarding relative thermodynamic stabilities, prediction of the free energy of activation and assistance in NMR signals assignments.

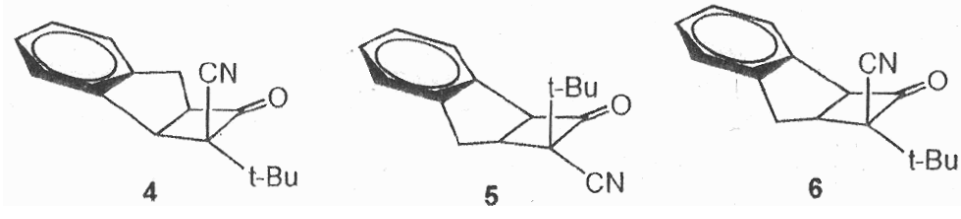


R_1 = (a) t-Bu; (b,c) C_6H_5S; (d) Cl; (e) CH_3; (f) C_6H_5
R_2 = (a) CN; (b) H; (c) CH_3; (d) Cl; (e) CH_3; (f) C_6H_5

Scheme 1

RESULTS AND DISCUSSION

The regio- and the stereospecificity of the cycloaddition of TBCK with indene yielding cyclobutanone **3a** is now unequivocally secured from the single-crystal X-ray diffraction determination and is illustrated in the ORTEP[11] representation in Figure 2. Additionally, one must note that the regio- and stereoisomers **4**, **5** and **6** have no signature in the NMR spectrum and GC/MS chromatogram of the crude reaction mixture, although all of them are more stable thermodynamically then cyclobutanone **3a**. Computations carried out at B3LYP/6-31G(d) level of theory[12a] predict that the *endo* cyclobutanone **3a** is less stable than *exo* **4** by $\Delta G = 2.5$ kcal/mol (273 K and 1 atm). The reverse regioisomers **5** and **6** are expected to be (within $\Delta G = 0.5 - 0.6$ kcal/mol) more stable than **3a**.



The *raison d'être* of the regiochemistry is straightforward if one assumes either a concerted or a stepwise mechanism for the cycloaddition. In principle, TBCK could add to indene double bond with the electrophilic C_α of ketene as the spearhead of the attack which brings into being a partially charged benzylic cation (like in **TS-1**) or a fully charged benzylic cation, like in the intermediate **I-1**. Therefore, C=O group lands in the closeness of the indene's CH_2. The reverse orientation of the cycloaddition would yield the less stable secondary cation (partially or fully charged).

The *endo* stereochemistry of the *t*-Bu group in cyclobutanone **3a** (*masochistic effect*[13]) is best understood if one tolerates a concerted mechanism of $_\pi2_s +_\pi2_a$[14a] topology or related.[14b] In the calculated transition state (B3LYP/6-31G(d)) TBCK adds orthogonal across the C=C bond of indene. The asynchronous transition state for this type of mechanism is illustrated in **TS-1** (see Figure 1). C_1-C_2 bond length (1.576 Å) is more advanced then C_{10}-C_{11} bond (2.464 Å). On the potential energy surface of TBCK cycloaddition with indene, **TS-1** turns out to be at $\Delta G^{\ddagger}$ = 20.0 kcal/mol (273 K and 1 atm) higher then cyclobutanone **3a**.

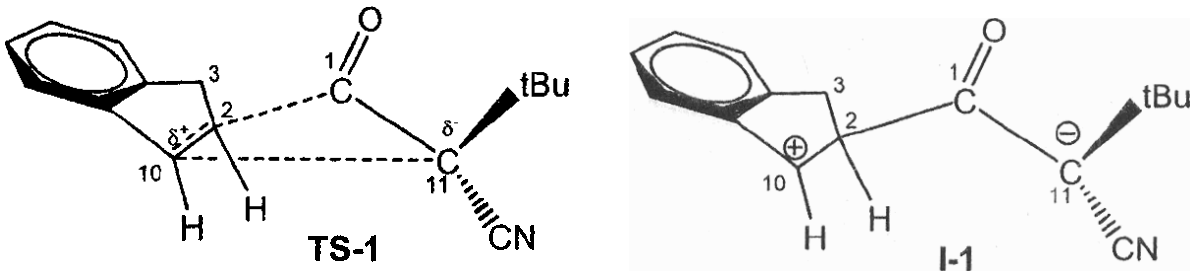


Fig. 1 – The transition state and the intermediate corresponding to the cyclobutanone **3a** formation

An analogue transition state (**TS-2**) yielding the cyclobutanone **4** is kinetically less favorable, and has a predicted (B3LYP/6-31G(d)) free energy of activation ($\Delta G^{\ddagger}$) of 36.7 kcal/mol (273 K and 1 atm). Additionally, the asynchronism of bonds formation is more apparent in **TS-2**. The newly formed C-C bonds length in **TS-2** (C_1-C_2: 1.834 Å; C_{10}-C_{11}: 3.099 Å) are longer than in **TS-1**, because of an earlier transition state.

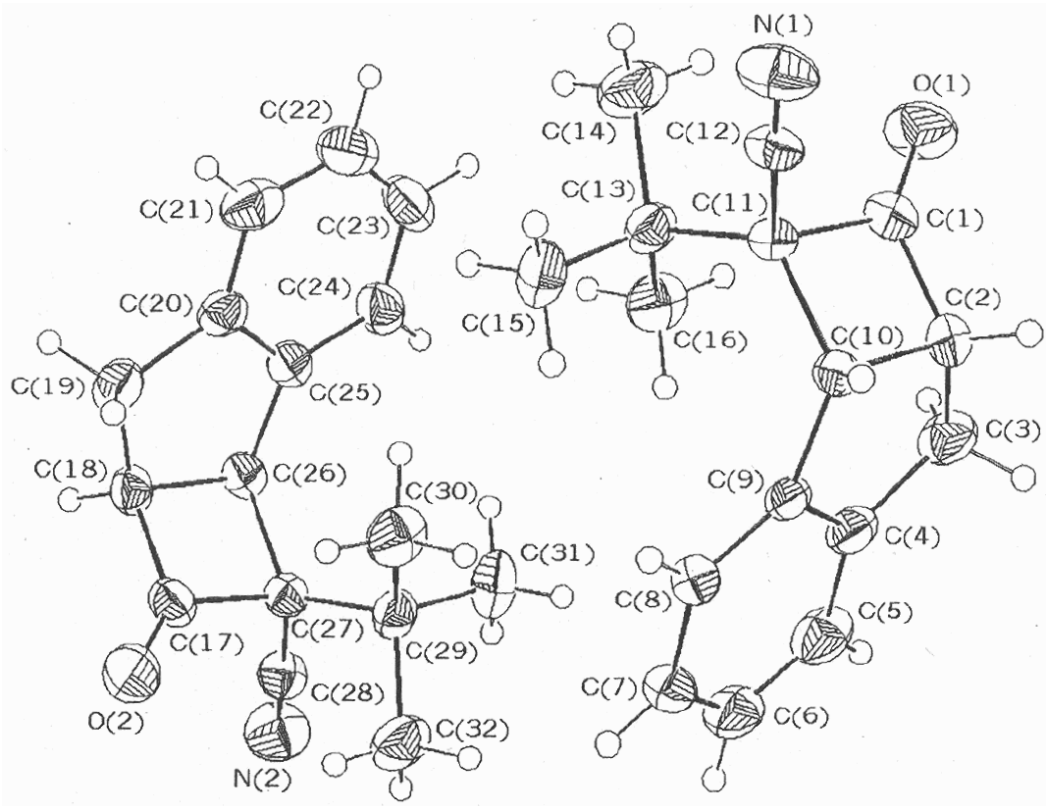
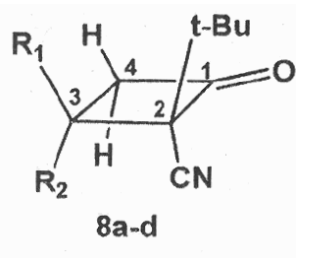


Fig. 2 – ORTEP representation of the two enantiomers of cyclobutanone **3a**.

The cyclobutanone 3a metrics. The rigidity of the polycyclic framework and the crowding around the four-membered rings constitute remarkable characteristics that are explicitly echoed in the cyclobutanones **3a** geometry. The most conspicuous is the 1.602 Å C_2-C_3 bond length that occurs between the bulky *t*-Bu group and the aromatic ring. The longest akin C-C bond in *t*-butylcyanocyclobutanones (see Tab. 1), turns out to be incorporated into the cyclobutanone **8a** resulted from styrene and TBCK.[3]



R_1 = (a) C_6H_5; (b) 1-naphthyl; (c) $(CH_2)_3OSi(CH_3)_2$t-Bu; (d) H
R_2 = (a) H; (b) H; (c) H; (d) p-CH_3O-C_6H_4

Fig. 3

Now, we would like to answer the question to what extent the longer C_2-C_3 bond length from cyclobutanone **3a** is topologically different from the same bond in the parent cyclobutanone. As expected intuitively, the electron density at bond critical point[12b,14c] is of lesser amount if the bond length is longer, while in both cases the bond has a cylindrical symmetry, as it is recognized by the value of bond ellipticity. The scrutiny of the topology of the C_{10}-C_{11} bond (see Figure 2) compared to the same bond (at calculated length of 1.56 Å) of cyclobutanone (values in parenthesis) by Bader's Atoms in Molecules[14c] protocol revealed that the at the bond critical point the electron density is $\rho = 0.20705$ eÅ^{-3} (0.23328), the laplacian $\nabla^2\rho$ is -0.38840 eÅ^{-5} (-0.50250) and the bond ellipticity (ε) is 0.02281 (0.00402).

Table 1

Relevant C-C bonds length (Å) of *t*-butylcyanocyclobutanones
(carbon numbering like in Figure 3, see references in text).

Cyclobutanone	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_1
8a	1.573	1.614	1.553	1.552
8b	1.556	1.608	1.552	1.497
8c	1.559	1.580	1.539	1.508
8d	1.554	1.591	1.548	1.490

Predicted bonds length (B3LYP/6-31G(d)) for the cyclobutanone ring **3a** presented in Fig. 4 are acceptable close to X-ray findings.

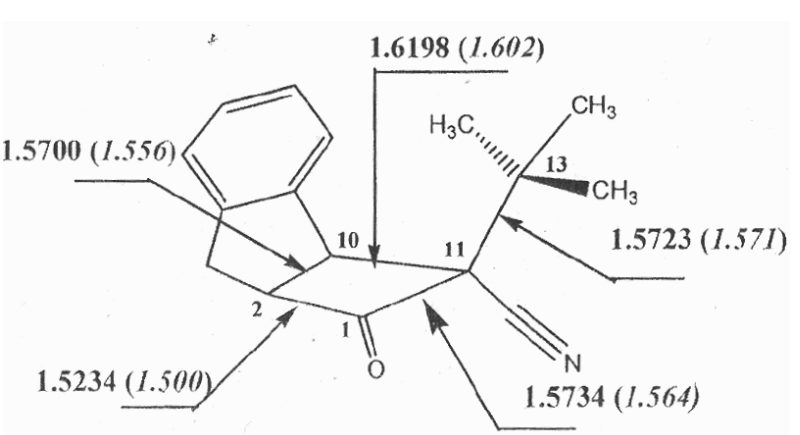


Fig. 4 – Calculated values (B3LYP/6-311++G(d,p)[12b]) *versus* X-ray bonds length (italic, in parentheses). Numbering of carbons is from Fig. 2.

Assignments of ^{1}H and ^{13}C NMR signals. Next, we have tested the ability of theoretical NMR shifts prediction (proton and carbon, TMS scale, GIAO isotropic shielding values) *versus* experimental results (see the Experimental section). The predicted proton chemical shifts for H^2, H^3*endo*, H^3*exo* and H^{10} protons in case the cyclobutanone **3a** and **4**, respectively have been computed with model chemistry B3LYP/6-31G(d). A good linear correlation, $\delta_{(GIAO,\ ppm)} = 0.9516*\delta_{(exp.,\ ppm)} + 0.697$ with R^2=0.9774, has resulted for the *endo*-cyclobutanone **3a**. The correlation of the GIAO chemical shifts of cyclobutanone **4** protons with the experimental values is of inferior quality (R^2=0.8885). It is gratifying that GIAO chemical shift calculation (implicitly signals assignment) can distinguish among *endo*- versus *exo* isomers. An additional benefit of the above mentioned correlation is the fact that one could credit the chemical shift at δ = 3.38 ppm to H^3*endo* proton and that at δ = 3.13 ppm to H^3*exo* proton. With the corresponding dihedral angles (Φ) pulled out from the B3LYP/6-31G(d) geometry, the $^3J_{H3,H2}$ coupling constants predicted by a simple Karplus equation[15] for the $H_{3endo}H_2$ (Φ =102.6°) is 2.9 Hz, (exp. 2.8 Hz), while $H_{3endo}H_2$ (Φ = 16.4°) is 8.7 Hz (exp. 11.8 Hz). For analytical purposes, one should note again, as in fact we have underlined in our previous publication,[16] that the proton H_{10}, *cis* to the CN group, is relatively deshielded (here δ = 4.60 ppm) compared to the chemical shift (δ = 4.46 ppm) of H_2.

Deceptively, the experiments with chemical shift reagents [Eu(fod)$_3$] revealed that the H_{10} has a greater molar induced shift (MIS) value, namely 3.99 compared to 3.01 of H_2. This result is counterintuitive, because the carbonyl group is a stronger Lewis base than the cyano group. Although we have not tested quantitatively the competition between carbonyl oxygen versus nitrogen from the cyano group, as we have done for other *t*-butylcyanocyclobutanones,[17] we believe that the complexation of the shift reagent occurs mostly at the nitrogen group, thus avoiding the steric crowding around the carbonyl oxygen which is augmented by the rigidity (lack of rotation of the substituent) of the cyclobutanone **3a** polycyclic system.

CONCLUSIONS

Single-crystal X-ray diffraction study of the cyclobutanone **3a**, the only isolated isomer, elucidates that the cycloaddition of TBCK with indene is regio- and stereospecific. Because the bulky *t*-Bu group is *cis* to the aromatic nucleus, the C-C bond flanked by those groups is elongated to 1.602 Å. The cyclobutanone ring is puckered. Calculations carried out at B3LYP/6-31G(d) level of theory predict that the order of thermodynamic stability of cylobutanone isomers is **4** > **6** > **5** > **3a**. The transition state of the cycloaddition of TBCK with indene to result cyclobutanone **3a** has computed free energy of activation of 22.0 kcal/mol and of 36.7 kcal/mol to computationally yield cyclobutanone **4**. NMR signals assignment for all protons and carbons chemical shifts were supported by the good correlation among GIAO calculated ^{1}H and ^{13}C NMR chemical shifts (on TMS scale) and the experimental results.

EXPERIMENTAL PART

Anhydrous benzene (CHIMOPAR, S.A., Bucharest) was dried over sodium wire. The 2,5-diazido- 3,6-di-t-butyl-1,4-benzoquinone has been synthesized starting from 2,5-di-*t*-butylhydroquinone according to the protocol developed by us.[18] The GC/MS analysis were run on Varian 3400, ion trap Varian Saturn 4D at 170 °C, injection port 260 °C, equipped with HP-5MS column (30 m; 0.25 mm ID). The initial oven temperature was set at 60 °C for 2 minutes and ramped to 280 °C with a gradient of 10 °C/minute). NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer.

2-*tert*-Butyl-1-oxo-2,2a,7,7a-tetrahydro-1*H*-cyclobut[*a*]indene-2-carbonitrile (3a). *t*-Butylcyanoketene was generated *in situ* by thermolysis of 2,5-diazido-3,6-di-t-butyl-1,4-benzoquinone in anhydrous benzene.[19] 1.0 g (3.3 mmoles) of 2,5-diazido-3,6-di-*t*-butyl-1,4-benzoquinone were decomposed in 25 mL anhydrous benzene at reflux temperature. A solution of 0.8 g (7.0 mmoles) of indene in 5 mL of anhydrous benzene was dropwise added over 20 minutes and followed by additional reflux for 4 hours. The solvent was removed and the crude reaction mixture was chromatographed on 100 g of silica (Merck, Si 60) with carbon tetrachloride to elute the traces of unreacted indene. A second fraction eluted with benzene (ca. 250 mL) contained the cyclobutanone **3a** (1.08 g 80%), mp. 117 °C (methanol). (calculated for $C_{16}H_{17}ON$ C, 80.30; H, 7.16 ; N, 5.85. Found: C, 80.40; H, 7.27; N, 5.67%). ^{1}H-NMR [$CDCl_3$, δ (ppm), J (Hz)]: 0.93 (s, 9H, t-Bu); 3.13 (dd, 17.3, 11.2, 1H, H^3); 3.38 (dd, 17.3; 2.8, 1H, H^3); 4.46 (ddd, 11.2; 9.2, 2.8; H^2); 4.60 (d, 9.2, H^{10}); 7.25 (m, 3H, $H^{5,6,7}$); 7.48 (dd, 2.5, 7.9; 1H, H^8). ^{13}C-NMR [($CDCl_3$, δ (ppm),]: 201.81 (C=O); 144.51 (C_4); 138.01 (C_9); 128.77 (C_5); 128.26 (C_8); 127.28 (C_6); 125.59 (C_7); 119.17 (C≡N); 71.25 (C_{11}) 61.18 (C_{10}); 49.89 (C_2); 36.39 (C_{13}); 33.41 (C_3); 26.39 (CH_3-*t*-Bu).

X-ray Diffraction Studies. Data collection and processing were carried out using a Bruker AXS SMART APEX system ("Babes-Bolyai" University, Cluj, Romania). Crystal of dimensions 0.43 x 0.27 x 0.21 mm, grown by slow evaporation of benzene at room temperature, was affixed to a cryo loop and optically centered. The data were collected on a Bruker AXS three-circle platform goniometer equipped with a CCD area detector with graphite-monochromated MoKα radiation (λ = 0.71073 Å at 297(2) K). The

structures were solved by direct methods SHELXS-97[20] and successive difference Fourier syntheses and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[21] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed at idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography.[22] The drawing was created with the ORTEP[11] program.

Table 2

Crystal data and structure refinement

Empirical formula	$C_{16}H_{17}NO$
Formula weight	239.31
Crystal system	monoclinic
Space group	P2(1)/c
Unit cell dimens (Å, deg)	a = 11.3653(10) ; b = 19.5566(17); c = 12.5335(11) α = 90; β = 107.788(2); γ = 90;
Volume	2652.6(4) $Å^3$
Z	8
Calculated density	1.198 Mg/m^3
Absorption coefficient	0.074 mm^{-1}
F(000)	1024
θ range for data collection	1.88 to 26.37 deg.
Limiting indices	$-14 \le h \le 14$; $-23 \le k \le 24$; $-15 \le l \le 15$
No. of reflns collected unique	21118
No. of indep refls	5386 [R(int) = 0.0517]
Compl to θ = 26.37	99.4 %
Max. and min. transmission	0.9845 and 0.9687
Data / restraints / parameters	5386 / 0 / 331
Goodness-of-fit on F^2	1.185
Final R indices [$I>2\sigma(I)$]	R1 = 0.0744; wR2 = 0.1495
Reflections collected / unique	21118 / 5386 [R(int) = 0.0517]
R indices (all data)	R1 = 0.0973, wR2 = 0.1594
Largest diff. peak and hole	0.176 and -0.171 e $Å^{-3}$

Table 3

Selected bond lengths [Å] and angles [deg] for cyclobutanone **3a**

C(1)-O(1)	1.189(3)
C(1)-C(2)	1.500(3)
C(1)-C(11)	1.564(3)
C(2)-C(3)	1.541(3)
C(2)-C(10)	1.556(3)
C(3)-C(4)	1.505(3)
C(9)-C(10)	1.504(3)
C(10)-C(11)	1.602(3)
C(11)-C(12)	1.462(3)
C(11)-C(13)	1.558(3)
C(12)-N(1)	1.140(3)
O(1)-C(1)-C(2)	134.0(2)
O(1)-C(1)-C(11)	131.9(2)
C(2)-C(1)-C(11)	94.14(16)
C(1)-C(2)-C(3)	117.1(2)
C(1)-C(2)-C(10)	89.57(16)
C(3)-C(2)-C(10)	107.13(17)
C(4)-C(3)-C(2)	104.18(18)
C(5)-C(4)-C(3)	127.4(2)
C(9)-C(4)-C(3)	112.73(19)
C(8)-C(9)-C(10)	128.64(19)
C(4)-C(9)-C(10)	110.50(19)
C(9)-C(10)-C(2)	105.01(17)
C(9)-C(10)-C(11)	122.00(17)
C(2)-C(10)-C(11)	90.56(15)
C(12)-C(11)-C(13)	109.82(18)
C(12)-C(11)-C(1)	109.05(17)
C(1)-C(11)-C(10)	85.69(15)
N(1)-C(12)-C(11)	178.3(3)

Table 4

Selected dihedral angles [deg] for cyclobutanone **3a**

O(1)-C(1)-C(2)-C(3)	-73.5(3)
C(11)-C(1)-C(2)-C(3)	107.6(2)
O(1)-C(1)-C(2)-C(10)	177.4(3)
C(11)-C(1)-C(2)-C(10)	-1.45(17)
C(1)-C(2)-C(3)-C(4)	-104.9(2)
C(10)-C(2)-C(3)-C(4)	-6.3(2)
C(2)-C(3)-C(4)-C(5)	-175.3(2)
C(2)-C(3)-C(4)-C(9)	3.9(3)
C(7)-C(8)-C(9)-C(10)	-178.0(2)
C(1)-C(2)-C(10)-C(9)	124.87(17)
C(1)-C(2)-C(10)-C(11)	1.42(16)
O(1)-C(1)-C(11)-C(12)	-69.1(3)
C(2)-C(1)-C(11)-C(12)	109.80(19)
O(1)-C(1)-C(11)-C(10)	-177.5(3)
C(2)-C(1)-C(11)-C(10)	1.42(16)
C(2)-C(10)-C(11)-C(1)	-1.36(15)
C(13)-C(11)-C(12)-N(1)	-160(8)
C(1)-C(11)-C(12)-N(1)	-31(8)

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