REVISED

Supporting Information for Photorearrangement of Vinylidenecyclopropanes to 1,2,3-Butatriene Derivatives

Kazuhiko Mizuno*, Hajime Maeda, Hikaru Sugita, Shogo Nishioka, Takayoshi Hirai, and Akira Sugimoto

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

mizuno@chem.osakafu-u.ac.jp

General.

Benzene was distilled from P_2O_5 then from Na. Methanol was distilled from Mg. Vinylidenecyclopropanes (**2a-h, j**) were prepared according to the literature,[4] and were used after purification by silica gel column chromatography and/or recrystallization.

Photoirradiation was performed by an Eikosha PIH-300 300W high-pressure mercury lamp through Pyrex filter. Melting points were determined on a Yanagimoto Micro Melting Point apparatus, Yanaco MP-500 and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX270 (270 MHz and 68 MHz, respectively) or a Varian MERCURY-300 (300 MHz and 75 MHz, respectively) spectrometer using Me_4Si as an internal standard. IR spectra were determined on a Jasco FT/IR-230 or a Jasco FT/IR-5000 spectrometer. UV-vis spectra were recorded on Jasco UVIDEC-670 or Shimadzu UV-160A spectrophotometer. Fluorescence spectra were taken on Jasco FP-770 spectrophotometer. Mass spectra (EI) were taken on a SHIMADZU GCMS-QP5050 operating in the electron impact mode (70 eV) equipped with DB-5MS column (J&W Scientific Inc., Serial: 8696181). HRMS spectra were obtained on a JEOL JMS-303H operating in the electron impact mode (70 eV) in Osaka Municipal Technical Research Institute. HPLC separations were performed on a recycling preparative HPLC equipped with Jasco PU-986 pump, Shodex RI-

72 differential refractometer, Megapak GEL 201Cp and 201CP columns (GPC) using $CHCl_3$ as an eluent. Column chromatography was conducted by using MERCK silica gel 60 (0.063-0.200 mm).

X-ray diffraction data of **3b** were collected by using Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) and a 18 kW rotating anode generator. Cell dimensions were obtained by least-square fitting from 20 high angle reflections. All computations for the structure determination were carried out on work station INDY (Silicon Graphics) using crystallographic program package TEXSAN. Details for X-ray crystallographic data is mentioned in X-ray structure report located at the end of this supporting information.

Photoreaction of 2a.

A benzene solution (10 mL) of 1-(2',2'-diphenylvinylidene)-2,2,3,3-tetramethyl-cyclopropane (**2a**, 82 mg, 0.30 mmol) was irradiated by a high-pressure mercury lamp through Pyrex filter under argon atmosphere. The reaction can be monitored by IR, UV, and NMR spectroscopy. After the all **2a** was consumed, solvent was removed in vacuo. Purification by a silica gel column chromatography (hexane) gave 1,1-diphenyl-4,5,5-trimethyl-1,2,3-hexatriene (**3a**, 45 mg, 55%) as colorless oil. **Data for 3a**: oil; ^1H NMR (270 MHz, $CDCl_3$) δ 7.25-7.52 (m, 10 H), 2.06 (s, 3 H), 1.21 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 150.8, 139.2, 139.1, 130.7, 128.8, 128.3, 127.2, 127.0, 116.7, 109.5, 104.3, 37.6, 29.3, 19.9; IR (neat) 2968, 2046, 1943, 1599, 1491, 1444, 768, 694 cm^{-1}; UV (cyclohexane) λ_{max} = 253, 340 nm; MS (EI) m/z = 165, 202, 216, 231, 244, 259, 274 (M^+); HRMS (EI) Calcd for $C_{21}H_{22}$: 274.1721. Found: 274.1787.

1,1-Bis(*p*-chlorophenyl)-4,5,5-trimethyl-1,2,3-hexatriene (3b)

Purified by silica gel column chromatography (hexane) then by recrystallization from methanol (85% yield). Mp 129-130 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.26-7.40 (m, 8 H), 2.06 (s, 3 H), 1.20 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 150.4, 137.4, 133.2, 132.7, 129.9, 129.5, 128.7, 128.6, 109.9, 109.3, 38.0, 29.5, 20.4; IR (neat) 2962, 2044, 1903, 1604,

1485 cm^{-1}; UV (cyclohexane) λ_{max} = 268, 345 nm; MS (EI) m/z = 343 (M^+).

1,1-Bis(*p*-methoxyphenyl)-4,5,5-trimethyl-1,2,3-hexatriene (3c)

Purified by silica gel column chromatography (hexane / ethyl acetate = 19 / 1) then by recycling preparative HPLC (45% yield). Oil; ^1H NMR (270 MHz, $CDCl_3$) δ 7.26-7.40 (m, 8 H), 2.06 (s, 3 H), 1.20 (s, 9 H).

1,1-Bis(*p*-methylphenyl)-4,5,5-trimethyl-1,2,3-hexatriene (3d)

Purified by silica gel column chromatography (hexane / ethyl acetate = 19 / 1) (62% yield). Oil; ^1H NMR (270 MHz, $CDCl_3$) δ 7.19-7.47 (m, 8 H), 2.42 (s, 6 H), 2.10 (s, 3 H), 1.26 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 146.0, 132.4, 131.8, 131.7, 124.4, 124.3, 124.1, 123.6, 33.0, 24.9, 16.9, 15.5; IR (neat) 2964, 2040, 1904, 1608, 1508 cm^{-1}; UV (cyclohexane) λ_{max} = 262, 344 nm.

Measurements of quantum yields

Quantum yields were determined by using a potassium ferrioxalate actinometer. The 313 nm Hg line was isolated through an aqueous K_2CrO_4 filter solution and Toshiba UV-29 glass filter. The intensity was calculated before actual photoreactions.

Trapping of diarylvinylidene carbene 5.

An ethyl vinyl ether solution (5 mL) of *cis*-1-(2',2'-diphenylvinylidene)-2,3-dimethylcyclopropane (**2g**, 39.0 mg, 0.16 mmol) was irradiated by a high-pressure mercury lamp through Pyrex filter under argon atmosphere for 1 h. The reaction mixture was evaporated and purified by silica gel column chromatography (hexane / benzene = 1 / 1) to give 1-(2',2'-diphenylvinylidene)-2-ethoxycyclopropane (**4a**, 10.4 mg, 25%). Spectral data of **4a-b** was identical with the authentic samples prepared in the precedent literature.[4]

X-ray report of 1,1-bis(*p*-chlorophenyl)-4,5,5-trimethyl-1,2,3-hexatriene (3b)

Experimental

Data Collection

A colorless prismatic crystal of $C_{21}H_{20}Cl_2$ having approximate dimensions of 0.30 x 0.40 x 0.50 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator.

Cell constants and an orientation matrix for data collection , obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $27.22 < 2\theta < 29.46°$ corresponded to a primitive monoclinic cell with dimensions:

a = 7.6341(9) $\AA$

b = 21.718(2) $\AA$ $\quad \beta = 97.61(1)°$

c = 11.394(2) $\AA$

V = 1872.6(4) $\AA^3$

For Z = 4 and F.W. = 343.29, the calculated density is 1.22 g/cm^3. The systematic absences of:

h0l: l $\neq$ 2n

0k0: k $\neq$ 2n

uniquely determine the space group to be:

$P2_1/c$ (#14)

The data were collected at a temperature of 23 $\pm$ 1°C using the ω-2θ scan technique to a maximum 2θ value of 55.1°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.33° with a take-off angle of 6.0°. Scans of (1.10 + 0.30 tan θ)° were made at a speed of 8.0°/min (in omega). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 5 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 258 mm, and the detector aperture was 9.0 x 13.0 mm (horizontal x vertical).

Data Reduction

Of the 4651 reflections which were collected, 4339 were unique (R_{int} = 0.018). The intensities of three representative reflection were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ, for Mo-Kα radiation is 3.4 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.97 to 1.00. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement[3] was based on 2077 observed reflections ($I > 3.00\sigma(I)$) and 288 variable parameters and converged (largest parameter shift was 0.06 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.043$$

$$R_w = \sqrt{(\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2)} = 0.056$$

The standard deviation of an observation of unit weight[4] was 1.88. The weighting scheme was based on counting statistics and included a factor (p = 0.035) to downweight the intense reflections. Plots of $\Sigma w(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.27 and -0.26 $e^-/\AA^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5] . Anomalous dispersion effects were included in Fcalc[6]; the values for Δf' and Δf" were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G. (1994). J. Appl. Cryst., in preparation.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized: $\Sigma w(|Fo| - |Fc|)^2$

where w = $\frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$

$\sigma_c(Fo)$ = e.s.d. based on counting statistics

p = p-factor

(4) Standard deviation of an observation of unit weight:

$$\sqrt{\Sigma w(|Fo| - |Fc|)^2/(No - Nv)}$$

where: No = number of observations

Nv = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{21}H_{20}Cl_2$
Formula Weight	343.29
Crystal Color, Habit	colorless, prismatic
Crystal Dimensions	0.30 X 0.40 X 0.50 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (27.2 - 29.5°)
Omega Scan Peak Width at Half-height	0.33°
Lattice Parameters	a = 7.6341(9)$\AA$ b = 21.718(2) $\AA$ c = 11.394(2) $\AA$ β = 97.61(1)°
	V = 1872.6(4) $\AA^3$
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.218 g/cm^3
F_{000}	720.00
μ(MoKα)	3.43 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	MoKα (λ = 0.71069 $\AA$) graphite monochromated

Attenuator	Zr foil (factors = 1.00, 3.55, 12.06, 42.89)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	258 mm
Temperature	23.0°C
Scan Type	ω-2θ
Scan Rate	8.0°/min (in ω) (up to 5 scans)
Scan Width	$(1.10 + 0.30 \tan \theta)°$
$2\theta_{max}$	55.1°
No. of Reflections Measured	Total: 4651 Unique: 4339 (R_{int} = 0.018)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9723 - 0.9990)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4} Fo^2]^{-1}$
p-factor	0.0350
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	2077
No. Variables	288
Reflection/Parameter Ratio	7.21
Residuals: R; Rw	0.043 ; 0.056
Goodness of Fit Indicator	1.88
Max Shift/Error in Final Cycle	0.06

Maximum peak in Final Diff. Map	0.27 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-0.26 $e^-/\AA^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Cl(1)	1.2143(1)	0.11344(5)	0.0467(1)	7.70(3)
Cl(2)	0.1971(1)	-0.18930(5)	0.1942(1)	8.21(3)
C(1)	0.5759(4)	0.0507(1)	0.2777(2)	4.03(7)
C(2)	0.5104(4)	0.0930(1)	0.3457(3)	4.54(7)
C(3)	0.4431(4)	0.1312(2)	0.4073(3)	5.08(8)
C(4)	0.3757(5)	0.1737(2)	0.4732(3)	5.67(9)
C(5)	0.2059(5)	0.1613(2)	0.5246(3)	6.25(10)
C(6)	0.0627(7)	0.2046(3)	0.4641(5)	8.0(1)
C(7)	0.2334(8)	0.1746(4)	0.6570(4)	9.7(2)
C(8)	0.1439(7)	0.0945(2)	0.5022(6)	8.1(1)
C(9)	0.4681(9)	0.2337(2)	0.4951(6)	8.7(2)
C(10)	0.7347(4)	0.0660(1)	0.2215(2)	3.87(7)
C(11)	0.7677(4)	0.1258(1)	0.1906(3)	4.61(8)
C(12)	0.9152(5)	0.1408(2)	0.1385(3)	5.30(9)
C(13)	1.0310(4)	0.0953(2)	0.1159(3)	4.80(8)
C(14)	1.0039(4)	0.0357(2)	0.1471(3)	4.77(8)
C(15)	0.8565(4)	0.0215(2)	0.1989(3)	4.42(8)
C(16)	0.4846(3)	-0.0088(1)	0.2565(2)	3.89(7)
C(17)	0.4858(4)	-0.0412(2)	0.1521(3)	4.43(8)
C(18)	0.3953(4)	-0.0954(2)	0.1307(3)	5.04(9)
C(19)	0.3049(4)	-0.1191(2)	0.2171(3)	5.15(8)
C(20)	0.3010(4)	-0.0886(2)	0.3221(3)	5.10(9)
C(21)	0.3891(4)	-0.0340(2)	0.3407(3)	4.44(8)
H(1)	0.048(6)	0.199(2)	0.379(5)	11(1)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(2)	0.114(6)	0.249(3)	0.466(4)	10(1)
H(3)	-0.039(7)	0.201(2)	0.493(4)	10(1)
H(4)	0.273(5)	0.221(2)	0.665(4)	7(1)
H(5)	0.133(7)	0.166(2)	0.684(4)	11(1)
H(6)	0.329(7)	0.146(2)	0.696(4)	12(1)
H(7)	0.045(7)	0.086(2)	0.534(4)	10(1)
H(8)	0.230(7)	0.068(2)	0.543(4)	11(1)
H(9)	0.136(8)	0.086(3)	0.415(5)	13(1)
H(10)	0.51(1)	0.243(4)	0.589(7)	20(1)
H(11)	0.555(7)	0.238(2)	0.459(4)	10(1)
H(12)	0.401(8)	0.264(3)	0.480(5)	12(1)
H(13)	0.684(4)	0.156(1)	0.204(2)	4.6(7)
H(14)	0.925(4)	0.182(2)	0.117(3)	6.4(8)
H(15)	1.085(4)	0.005(1)	0.133(2)	4.6(7)
H(16)	0.836(3)	-0.015(1)	0.219(2)	3.6(6)
H(17)	0.538(3)	-0.025(1)	0.093(2)	4.1(6)
H(18)	0.398(4)	-0.117(1)	0.058(3)	5.5(8)
H(19)	0.248(5)	-0.105(2)	0.381(3)	6.7(9)
H(20)	0.390(3)	-0.015(1)	0.409(2)	4.2(7)

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	0.0741(6)	0.1023(8)	0.1254(9)	-0.0090(5)	0.0472(6)	0.0238(6)
Cl(2)	0.0896(7)	0.0982(8)	0.1291(9)	-0.0416(6)	0.0337(6)	-0.0288(7)
C(1)	0.049(2)	0.060(2)	0.045(2)	0.007(1)	0.009(1)	0.003(1)
C(2)	0.054(2)	0.063(2)	0.056(2)	0.004(2)	0.014(1)	0.005(2)
C(3)	0.066(2)	0.067(2)	0.064(2)	0.014(2)	0.022(2)	0.008(2)
C(4)	0.079(2)	0.072(2)	0.068(2)	0.020(2)	0.020(2)	0.002(2)
C(5)	0.068(2)	0.102(3)	0.070(2)	0.033(2)	0.019(2)	0.000(2)
C(6)	0.087(3)	0.110(4)	0.103(4)	0.041(3)	0.000(3)	-0.003(3)
C(7)	0.088(4)	0.205(7)	0.081(3)	0.042(4)	0.029(3)	-0.003(4)
C(8)	0.083(3)	0.093(4)	0.142(5)	0.016(3)	0.055(3)	0.023(3)
C(9)	0.124(4)	0.069(3)	0.148(5)	0.000(3)	0.052(4)	-0.025(3)
C(10)	0.049(2)	0.057(2)	0.041(2)	0.002(1)	0.007(1)	0.001(1)
C(11)	0.062(2)	0.051(2)	0.064(2)	0.005(2)	0.015(2)	0.001(2)
C(12)	0.074(2)	0.056(2)	0.074(2)	-0.008(2)	0.020(2)	0.010(2)
C(13)	0.052(2)	0.070(2)	0.063(2)	-0.006(2)	0.018(1)	0.008(2)
C(14)	0.052(2)	0.064(2)	0.068(2)	0.008(2)	0.017(2)	0.008(2)
C(15)	0.055(2)	0.053(2)	0.062(2)	0.000(2)	0.015(1)	0.013(2)
C(16)	0.040(1)	0.060(2)	0.049(2)	0.007(1)	0.009(1)	0.005(1)
C(17)	0.053(2)	0.071(2)	0.047(2)	0.001(2)	0.013(1)	0.003(2)
C(18)	0.058(2)	0.077(2)	0.056(2)	-0.003(2)	0.006(2)	-0.011(2)
C(19)	0.047(2)	0.071(2)	0.078(2)	-0.009(2)	0.010(2)	-0.008(2)
C(20)	0.050(2)	0.080(3)	0.068(2)	-0.008(2)	0.020(2)	0.003(2)
C(21)	0.049(2)	0.072(2)	0.050(2)	0.000(2)	0.012(1)	-0.003(2)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table 3. Bond Lengths($\AA$)

atom	atom	distance	atom	atom	distance
Cl(1)	C(13)	1.740(3)	Cl(2)	C(19)	1.736(3)
C(1)	C(2)	1.341(4)	C(1)	C(10)	1.481(4)
C(1)	C(16)	1.474(4)	C(2)	C(3)	1.241(4)
C(3)	C(4)	1.334(4)	C(4)	C(5)	1.515(5)
C(4)	C(9)	1.489(6)	C(5)	C(6)	1.535(5)
C(5)	C(7)	1.523(6)	C(5)	C(8)	1.536(6)
C(6)	H(1)	0.97(5)	C(6)	H(2)	1.04(5)
C(6)	H(3)	0.89(5)	C(7)	H(4)	1.04(4)
C(7)	H(5)	0.88(5)	C(7)	H(6)	1.01(5)
C(8)	H(7)	0.90(5)	C(8)	H(8)	0.95(5)
C(8)	H(9)	1.00(6)	C(9)	H(10)	1.09(7)
C(9)	H(11)	0.83(5)	C(9)	H(12)	0.83(6)
C(10)	C(11)	1.377(4)	C(10)	C(15)	1.388(4)
C(11)	C(12)	1.381(4)	C(11)	H(13)	0.95(3)
C(12)	C(13)	1.373(5)	C(12)	H(14)	0.92(3)
C(13)	C(14)	1.365(4)	C(14)	C(15)	1.373(4)
C(14)	H(15)	0.94(3)	C(15)	H(16)	0.85(3)
C(16)	C(17)	1.384(4)	C(16)	C(21)	1.391(4)
C(17)	C(18)	1.370(4)	C(17)	H(17)	0.89(3)
C(18)	C(19)	1.375(4)	C(18)	H(18)	0.95(3)
C(19)	C(20)	1.371(4)	C(20)	C(21)	1.367(4)
C(20)	H(19)	0.90(3)	C(21)	H(20)	0.88(3)

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	C(1)	C(10)	119.1(3)	C(2)	C(1)	C(16)	119.4(3)
C(10)	C(1)	C(16)	121.5(2)	C(1)	C(2)	C(3)	177.5(3)
C(2)	C(3)	C(4)	177.9(4)	C(3)	C(4)	C(5)	120.6(3)
C(3)	C(4)	C(9)	119.3(4)	C(5)	C(4)	C(9)	120.1(3)
C(4)	C(5)	C(6)	108.2(4)	C(4)	C(5)	C(7)	109.7(4)
C(4)	C(5)	C(8)	111.3(3)	C(6)	C(5)	C(7)	109.0(4)
C(6)	C(5)	C(8)	108.5(4)	C(7)	C(5)	C(8)	110.0(5)
C(5)	C(6)	H(1)	110(2)	C(5)	C(6)	H(2)	108(2)
C(5)	C(6)	H(3)	112(3)	H(1)	C(6)	H(2)	97(3)
H(1)	C(6)	H(3)	111(4)	H(2)	C(6)	H(3)	115(4)
C(5)	C(7)	H(4)	105(2)	C(5)	C(7)	H(5)	107(3)
C(5)	C(7)	H(6)	108(2)	H(4)	C(7)	H(5)	115(4)
H(4)	C(7)	H(6)	110(3)	H(5)	C(7)	H(6)	109(4)
C(5)	C(8)	H(7)	112(3)	C(5)	C(8)	H(8)	108(2)
C(5)	C(8)	H(9)	108(3)	H(7)	C(8)	H(8)	104(4)
H(7)	C(8)	H(9)	114(4)	H(8)	C(8)	H(9)	108(4)
C(4)	C(9)	H(10)	113(4)	C(4)	C(9)	H(11)	114(3)
C(4)	C(9)	H(12)	112(4)	H(10)	C(9)	H(11)	109(5)
H(10)	C(9)	H(12)	97(5)	H(11)	C(9)	H(12)	108(5)
C(1)	C(10)	C(11)	120.6(3)	C(1)	C(10)	C(15)	122.1(3)
C(11)	C(10)	C(15)	117.3(3)	C(10)	C(11)	C(12)	121.3(3)
C(10)	C(11)	H(13)	117(1)	C(12)	C(11)	H(13)	120(1)
C(11)	C(12)	C(13)	119.5(3)	C(11)	C(12)	H(14)	116(2)
C(13)	C(12)	H(14)	124(2)	Cl(1)	C(13)	C(12)	119.9(3)

Table 4. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	C(13)	C(14)	119.4(2)	C(12)	C(13)	C(14)	120.7(3)
C(13)	C(14)	C(15)	119.1(3)	C(13)	C(14)	H(15)	120(1)
C(15)	C(14)	H(15)	120(1)	C(10)	C(15)	C(14)	122.0(3)
C(10)	C(15)	H(16)	116(1)	C(14)	C(15)	H(16)	121(1)
C(1)	C(16)	C(17)	122.0(3)	C(1)	C(16)	C(21)	120.8(3)
C(17)	C(16)	C(21)	117.2(3)	C(16)	C(17)	C(18)	121.9(3)
C(16)	C(17)	H(17)	120(1)	C(18)	C(17)	H(17)	117(1)
C(17)	C(18)	C(19)	118.9(3)	C(17)	C(18)	H(18)	120(1)
C(19)	C(18)	H(18)	120(1)	Cl(2)	C(19)	C(18)	119.6(3)
Cl(2)	C(19)	C(20)	119.4(3)	C(18)	C(19)	C(20)	121.0(3)
C(19)	C(20)	C(21)	119.2(3)	C(19)	C(20)	H(19)	121(2)
C(21)	C(20)	H(19)	119(2)	C(16)	C(21)	C(20)	121.7(3)
C(16)	C(21)	H(20)	118(1)	C(20)	C(21)	H(20)	119(1)

Table 5. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Cl(1)	C(13)	C(12)	C(11)	178.3(3)	Cl(1)	C(13)	C(14)	C(15)	-178.3(2)
Cl(2)	C(19)	C(18)	C(17)	-177.3(2)	Cl(2)	C(19)	C(20)	C(21)	178.7(2)
C(1)	C(2)	C(3)	C(4)	-153(7)	C(1)	C(10)	C(11)	C(12)	179.9(3)
C(1)	C(10)	C(15)	C(14)	-179.8(3)	C(1)	C(16)	C(17)	C(18)	-177.5(3)
C(1)	C(16)	C(21)	C(20)	178.9(3)	C(2)	C(1)	C(10)	C(11)	-30.1(4)
C(2)	C(1)	C(10)	C(15)	149.2(3)	C(2)	C(1)	C(16)	C(17)	148.7(3)
C(2)	C(1)	C(16)	C(21)	-29.7(4)	C(2)	C(3)	C(4)	C(5)	-178(9)
C(2)	C(3)	C(4)	C(9)	2(10)	C(3)	C(2)	C(1)	C(10)	148(7)
C(3)	C(2)	C(1)	C(16)	-29(7)	C(3)	C(4)	C(5)	C(6)	-112.8(4)
C(3)	C(4)	C(5)	C(7)	128.4(5)	C(3)	C(4)	C(5)	C(8)	6.4(5)
C(6)	C(5)	C(4)	C(9)	66.7(5)	C(7)	C(5)	C(4)	C(9)	-52.1(6)
C(8)	C(5)	C(4)	C(9)	-174.1(5)	C(10)	C(1)	C(16)	C(17)	-28.8(4)
C(10)	C(1)	C(16)	C(21)	152.8(3)	C(10)	C(11)	C(12)	C(13)	0.5(5)
C(10)	C(15)	C(14)	C(13)	-0.6(5)	C(11)	C(10)	C(1)	C(16)	147.4(3)
C(11)	C(10)	C(15)	C(14)	-0.4(4)	C(11)	C(12)	C(13)	C(14)	-1.6(5)
C(12)	C(11)	C(10)	C(15)	0.5(5)	C(12)	C(13)	C(14)	C(15)	1.7(5)
C(15)	C(10)	C(1)	C(16)	-33.3(4)	C(16)	C(17)	C(18)	C(19)	-1.9(5)
C(16)	C(21)	C(20)	C(19)	-0.8(5)	C(17)	C(16)	C(21)	C(20)	0.5(4)
C(17)	C(18)	C(19)	C(20)	1.5(5)	C(18)	C(17)	C(16)	C(21)	0.9(4)
C(18)	C(19)	C(20)	C(21)	-0.2(5)					

Table 6. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC
Cl(1)	H(12)	3.16(6)	65404
Cl(1)	H(17)	3.25(3)	75503
Cl(2)	H(5)	3.07(5)	55603
Cl(2)	H(1)	3.11(5)	54502
Cl(2)	H(3)	3.32(5)	54502
Cl(2)	C(6)	3.398(5)	54502
C(1)	H(8)	3.49(5)	65603
C(2)	H(19)	3.42(3)	65603
C(3)	H(20)	3.41(3)	65603
C(4)	H(19)	3.46(3)	65603
C(8)	H(19)	3.44(4)	55603
C(9)	H(18)	3.47(3)	65502
C(10)	H(9)	3.56(6)	65501
C(11)	H(1)	3.24(5)	65501
C(12)	H(1)	3.06(5)	65501
C(12)	H(2)	3.56(5)	65404
C(13)	H(9)	3.41(6)	65501
C(14)	H(9)	3.28(6)	65501
C(15)	H(9)	3.35(6)	65501
C(16)	H(8)	3.21(5)	65603
C(17)	H(6)	3.09(5)	65603
C(17)	H(15)	3.20(3)	45501
C(18)	H(15)	3.22(3)	45501
C(19)	H(15)	3.25(3)	45501
Cl(1)	H(2)	3.19(6)	65404
Cl(1)	H(18)	3.34(3)	75503
Cl(2)	H(2)	3.10(5)	54502
Cl(2)	H(11)	3.16(5)	64502
Cl(2)	H(10)	3.34(8)	65603
Cl(2)	H(14)	3.55(3)	65503
C(2)	H(20)	3.27(3)	65603
C(3)	H(19)	3.20(3)	65603
C(3)	C(20)	3.548(5)	65603
C(6)	H(14)	3.28(4)	45504
C(8)	H(16)	3.60(3)	65603
C(10)	H(18)	3.40(3)	65503
C(11)	H(18)	2.96(3)	65503
C(11)	H(10)	3.58(8)	55404
C(12)	H(18)	3.10(3)	65503
C(12)	H(9)	3.58(6)	65501
C(13)	H(15)	3.59(3)	75503
C(14)	H(15)	3.29(3)	75503
C(16)	H(15)	3.20(3)	45501
C(16)	H(6)	3.32(6)	65603
C(17)	H(17)	3.13(3)	65503
C(18)	H(6)	2.91(5)	65603
C(19)	H(6)	2.90(5)	65603
C(20)	H(6)	3.12(6)	65603

Table 6. Non-bonded Contacts out to 3.60 Å (continued)

atom	atom	distance	ADC
C(20)	H(15)	3.24(3)	45501
C(21)	H(8)	3.12(5)	65603
C(21)	H(20)	3.29(3)	65603
H(1)	H(14)	3.03(6)	45501
H(2)	H(14)	2.82(6)	45504
H(3)	H(19)	3.09(6)	55603
H(4)	H(14)	3.39(5)	45504
H(5)	H(16)	3.46(6)	65603
H(6)	H(18)	3.32(6)	65603
H(7)	H(19)	2.58(6)	55603
H(8)	H(16)	3.04(5)	65603
H(10)	H(13)	2.80(8)	4
H(10)	H(14)	3.56(8)	4
H(11)	H(18)	3.18(6)	65502
H(12)	H(18)	3.07(6)	65502
H(13)	H(18)	3.09(4)	65503
H(15)	H(15)	3.14(5)	75503
H(20)	H(20)	2.57(6)	65603
C(20)	H(7)	3.29(5)	55603
C(21)	H(15)	3.20(3)	45501
C(21)	H(6)	3.31(6)	65603
H(1)	H(13)	3.33(6)	45501
H(3)	H(14)	2.95(6)	45504
H(3)	H(11)	3.18(7)	45501
H(5)	H(19)	3.19(6)	55603
H(6)	H(16)	3.31(6)	65603
H(6)	H(19)	3.57(7)	65603
H(7)	H(16)	3.24(5)	65603
H(8)	H(20)	3.10(6)	65603
H(10)	H(19)	3.54(9)	65603
H(10)	H(18)	3.58(9)	65502
H(11)	H(14)	3.59(6)	4
H(12)	H(13)	3.57(6)	4
H(14)	H(18)	3.28(5)	65503
H(17)	H(17)	2.40(5)	65503

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus ± 4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1)	X,	Y,	Z	(2)	-X,	1/2+Y,	1/2-Z
(3)	-X,	-Y,	-Z	(4)	X,	1/2-Y,	1/2+Z