05 April 2018 "Uncle Al" < *xroqus* {} *gmail.com* >

http://www.mazepath.com/uncleal/EquivPrinFail.pdf

Dark matter**[1**], Milgrom acceleration, Tully-Fisher relation; baryogenesis, non-classical gravitation, Chern-Simons repair of Einstein-Hilbert action; SUSY (proton decay**[2]**) all share common mode failure. Postulated *exact* vacuum mirror symmetry may not be *exact*. Detect and measure the divergence in one day.

Massless boson photons detect no vacuum refraction, dispersion, dissipation, dichroism, or gyrotropy. Postulating contingent vacuum symmetries are *exactly* true for fermionic matter (quarks, hadrons) obtains prediction failures consistent with vacuum trace chiral anisotropy selective to hadrons**[3]**.

1. Big Bang matter and antimatter must *exactly* cancel. Noether's theorems couple exact symmetries with *exact* conservation laws. Matter visibly exists in excess of antimatter.
2. Baryogenesis**[4]** requires Sakharov conditions: trace broken spatial mirror symmetry.
3. Einstein-Cartan gravitation contains achiral spacetime curvature plus chiral spacetime torsion**[5,6]**; "vacuum structure and the dynamics of chiral symmetry breaking"**[7]**.
4. Vacuum has consequential trace background chiral anisotropy toward hadrons.
5. Enantiomorphs (opposite shoes) embed within chiral vacuum background (mount a left foot) with different energies. Extreme geometrically chiral-divergent test masses vacuum free fall along non-identical minimum action trajectories, violating the Equivalence Principle.
6. Fifty years of non-physical physical theory celebrate process absent product. Electroweak consequences are left-handed toward matter. **Test spacetime geometry with geometry[8]**.

Exact vacuum isotropy Noetherean couples with *exact* angular momentum conservation. Trace chiral anisotropy leaks 1.2×10^{-10} m/s^2 Milgrom acceleration**[9]**. Tully-Fisher is not dark matter. Baryogenesis is 6.1×10^{-10} bias, hadrons less antihadrons versus photons. The cosmological constant appears**[10].**

Defective postulates cannot be exposed when derivation defines observation. No classical, relativistic, quantum mechanical; composition, field, spin, orbit observation qualifies. Test for explicit vacuum chiral symmetry breaking selective to hadrons**[11]**, falsifying accepted but empirically sterile theory.

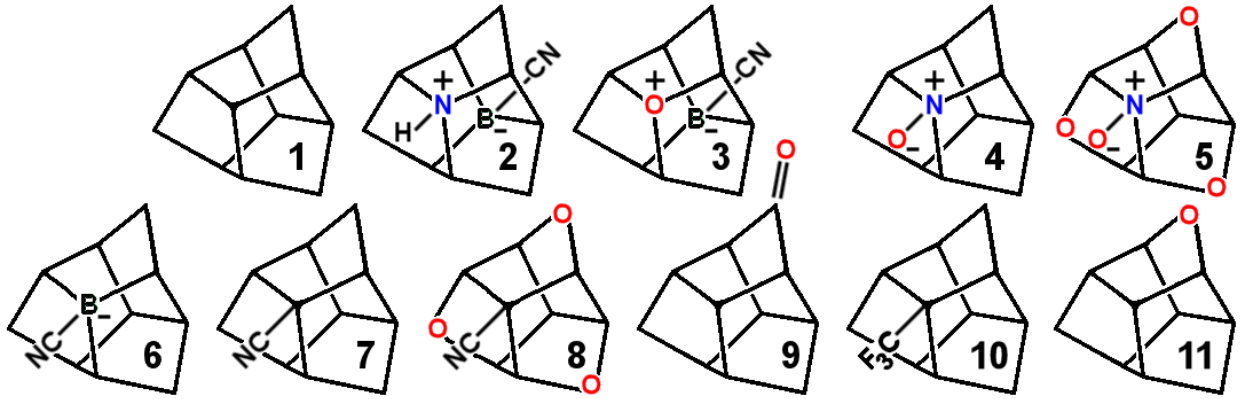
Molecular geometric test masses are chemically identical non-superposable mirror images, opposite shoes, enantiomers. They embed within a vacuum left foot – trace chiral anisotropy toward hadrons – with different energies. Molecular vibrational transitions are excluded below ~100 kelvin. Rotational transitions are ΔE 3 - 300 GHz, 0.144 - 14.4 kelvin, 0.000286 - 0.0286 kcal/mole, 0.1 – 10 cm^{-1}. Extreme enantiomers' deep cryogenic microwave rotational spectra are *exactly* identical and *exactly* superposed, in theory. Test assumed theory with observation. Look.

Enantiomers' geometric chiral divergence cannot be measured. It is calculable, CHI = 0 (achiral) to CHI = 1 (perfect geometric chiral divergence)**[12,13,14]**. Molecular reduction to practice includes

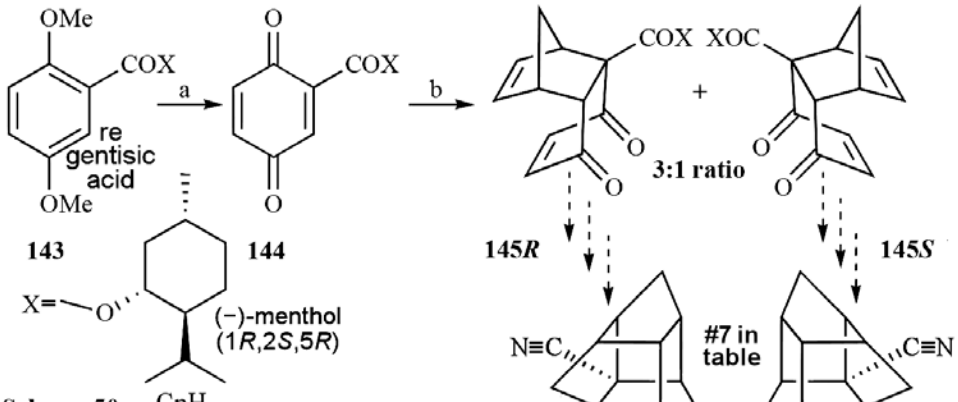
1. **Large dipole moment** Strong microwave rotational transitions require large dipole moments.
2. **Volatility** A molecular beam must be formed, propagate, and be manipulated.
3. **Stability** Molecules must not rearrange, react, or fragment during launch, processing, detection.
4. **Rotational symmetry** Point group $\boldsymbol{C}_3$ prolate symmetric tops give distinct spectra.
5. **Extreme geometric chiral divergence** CHI is calculated. Product 1:1 enantiomer ratio can be skewed, spectral intensity then allowing enantiomer identification. The bulky chiral auxilliary directs Diels-Alder cycloaddition to the desired *endo*-configuration, then becomes the –CN.

There is literature bulk synthesis of $\boldsymbol{D}_3$-trishomocuban-2-carbonitrile, 2-cyano-$\boldsymbol{D}_3$-trishomocubane, pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-2-carbonitrile**[15,16].** Facile high yield syntheses of *O*,*O*-dimethyl gentisic acid bulky chiral esters ((–)-menthol, (–)-borneol, (+)-fenchol) may proceed by direct sodium metallation of 1,4-dimethoxybenzene**[17]** (or n-BuLi/TMEDA/THF + HMPA), then react with

alcohol chloroformates**[18].** Ammonolyze (NH_3/imidazole) the ester, dehydrate (T3P**[19,20]**), R-CN. Menthyl ester product is saponified to the free R-COOH, then SF_4 to R-CF_3**[21.22,23]**.



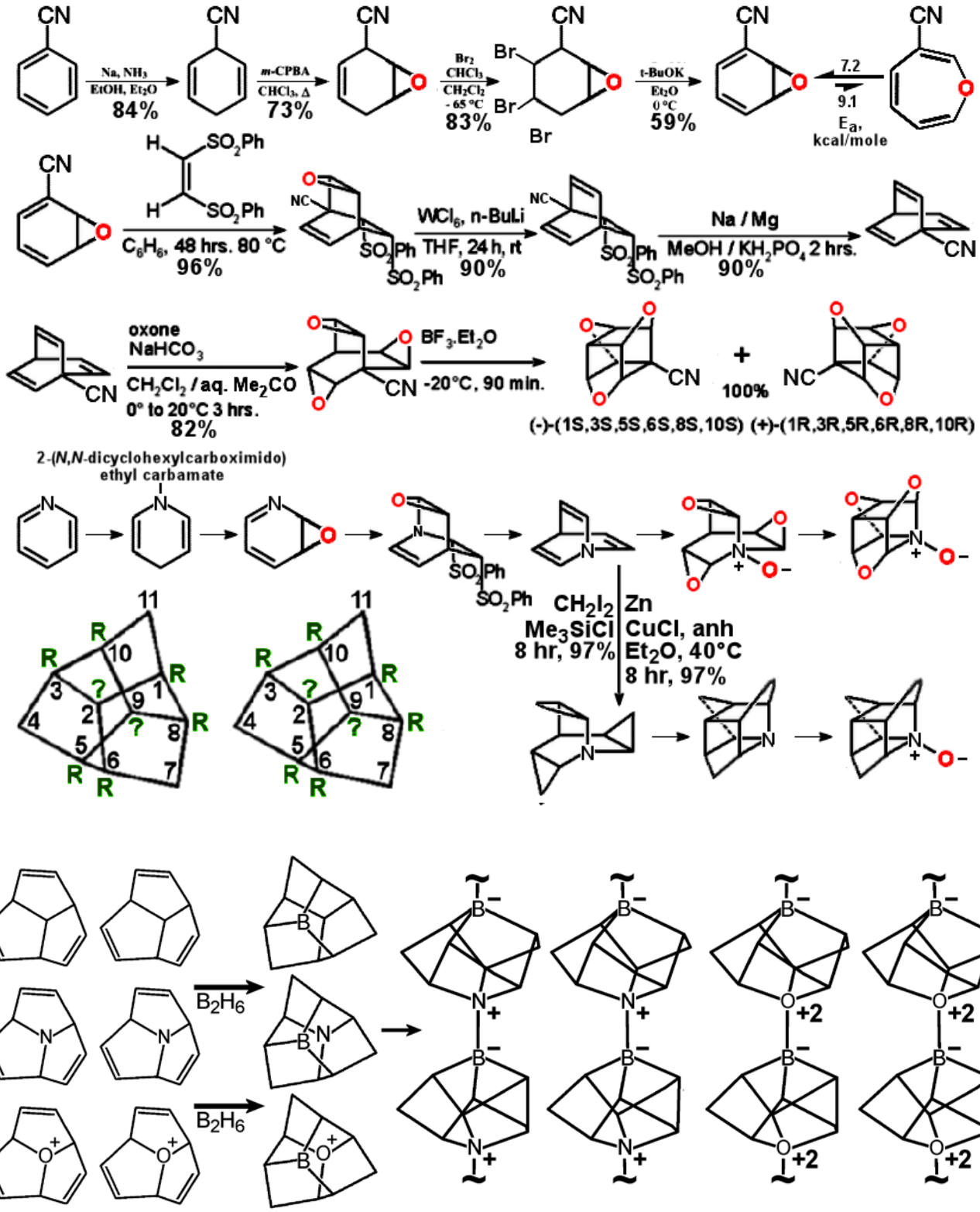
	Molecule (**Prolate rotors**)	Formula	CHI	Moments of Inertia, amu-Å^2 (HyperChem)			Dipole, debyes
	phenylalanine, vacuum	$C_9H_{11}NO_2$	0.058600	I_x	I_y	I_z	4.9
1	hydrocarbon	$C_{11}H_{14}$	0.628218	282.518	282.518	384.000	0.0
2	**2-ammonium-9-cyanoboride**	**$C_{10}H_{13}BN_2$**	**0.896704**	**374.493**	**538.365**	**538.365**	**23.**
3	2-oxonium-9-cyanoboride	$C_{10}H_{12}BNO$	0.825124	368.600	536.117	536.117	23
4	2-amine oxide	$C_{10}H_{13}NO$	0.659166	369.364	369.364	374.320	5.0
5	**2-amine oxide-4,7,11-trioxa**	**$C_7H_7NO_4$**	**0.995919**	**350.034**	**352.833**	**352.833**	**5.0**
6	**2-cyanoboride**	**$C_{11}H_{13}N$**	**0.905982**	**395.966**	**571.005**	**571.005**	**4.5**
7	**2-cyano *best first observation***	**$C_{12}H_{13}N$**	**0.884725**	**384.270**	**536.973**	**536.973**	**4.2**
8	**2-cyano-4,7,11-trioxa**	**$C_9H_7NO_3$**	**0.850460**	**359.196**	**521.900**	**521.900**	**4.1**
9	4-oxo	$C_{11}H_{12}O$	0.648576	282.018	421.039	523.570	3.3
10	**2-trifluoromethyl *also good***	**$C_{12}H_{13}F_3$**	**0. 915777**	**479.482**	**817.450**	**817.450**	**2.0**
11	4-oxa	$C_{10}H_{12}O$	0.712524	274.348	278.637	375.450	1.8

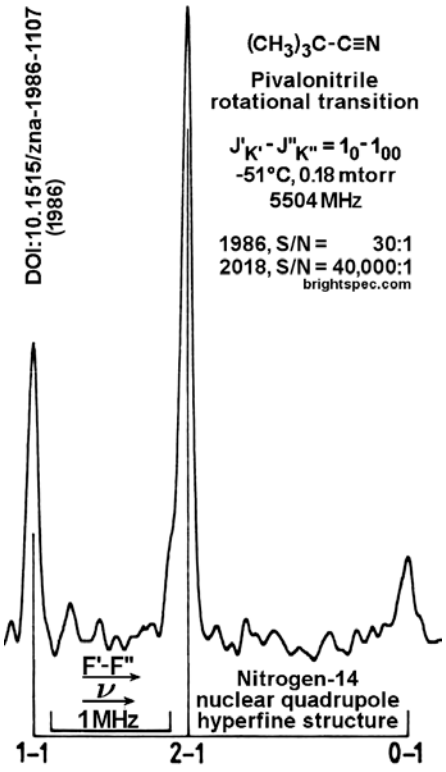


Scheme 50.
a) Ag_2O_2, HNO_3, dioxane, 10 min, 89%;
b) CpH, CH_2Cl_2, $ZnCl_2$, −78°C, 3 hrs., 80%.

Curr. Org. Chem. **16**(22), 2623 (2012), DOI: 10.2174/138527212804004508
Tetrahedron **54**(20), 5363 (1998), DOI: 10.1016/S0040-4020(98)00211-7

Heterocyclic analogues are assembled differently**[24,25,26,27,28,29,30]**. Removing six >CH_2 methylene hydrogens for three >O ether oxygens aids volatility. Lofting amine oxide into vacuum may go poorly. Mere $(CH_3)_3N^+ - O^-$ melts at 220 °C, plus thermal deoxygenation concerns.





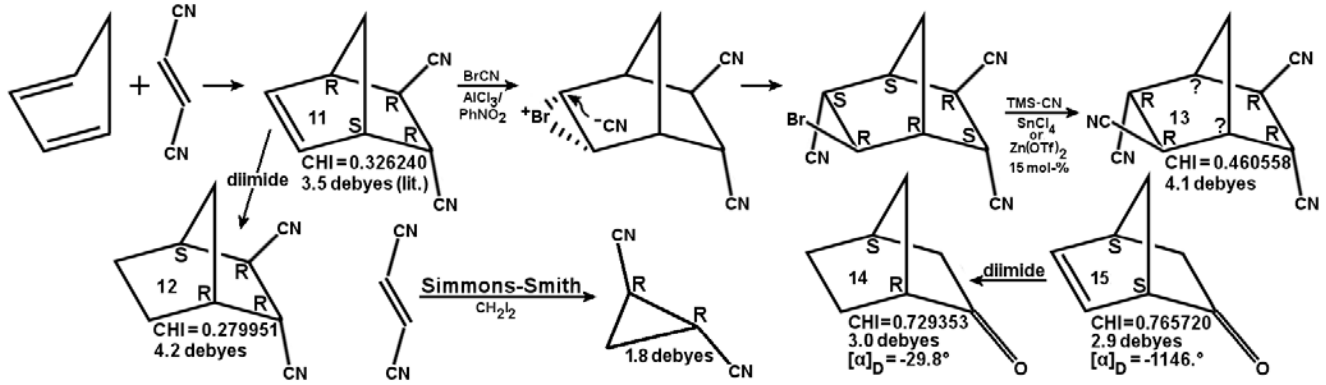
Slowing, trapping, and cooling uncharged polar molecules is hard. Bulk charged molecules have counterions and low vapor pressure. Vacuum-phase tertiary amine**[31,32]** protonates into a cation; tertiary borane**[33]** dative bonds with fluoride or cyanide into an anion. They do not add independently rotatable moieties. 2-aza-9-bora mixed heterocycle assembles into a self-healing frustrated Lewis pair**[34]** linear high polymer reverting to monomer by protic acid, cyanide, fluoride, or thermal dissociation,. Axial compression and internal delocalization of charge suggest a new class of organic conductors. Strongly coupling light atom skeleton phonons to internal electron density hints a BCS superconductor.

Vacuum supersonic expansion affords rotational temperatures ~5 kelvin with vibrational spectra frozen out. Chirped-pulse Fourier transform microwave spectrometry[**35,36,37]** then exquisitely outputs self-calibrated rotational spectra (augmented by nitrogen-14 nuclear quadrupole hyperfine coupling**[38,39]**) of the ~3:1 *R*:*S* enantiomer mixture). Observation exceeds instrument resolution through spectral line shape and hyperfine coupling lines.

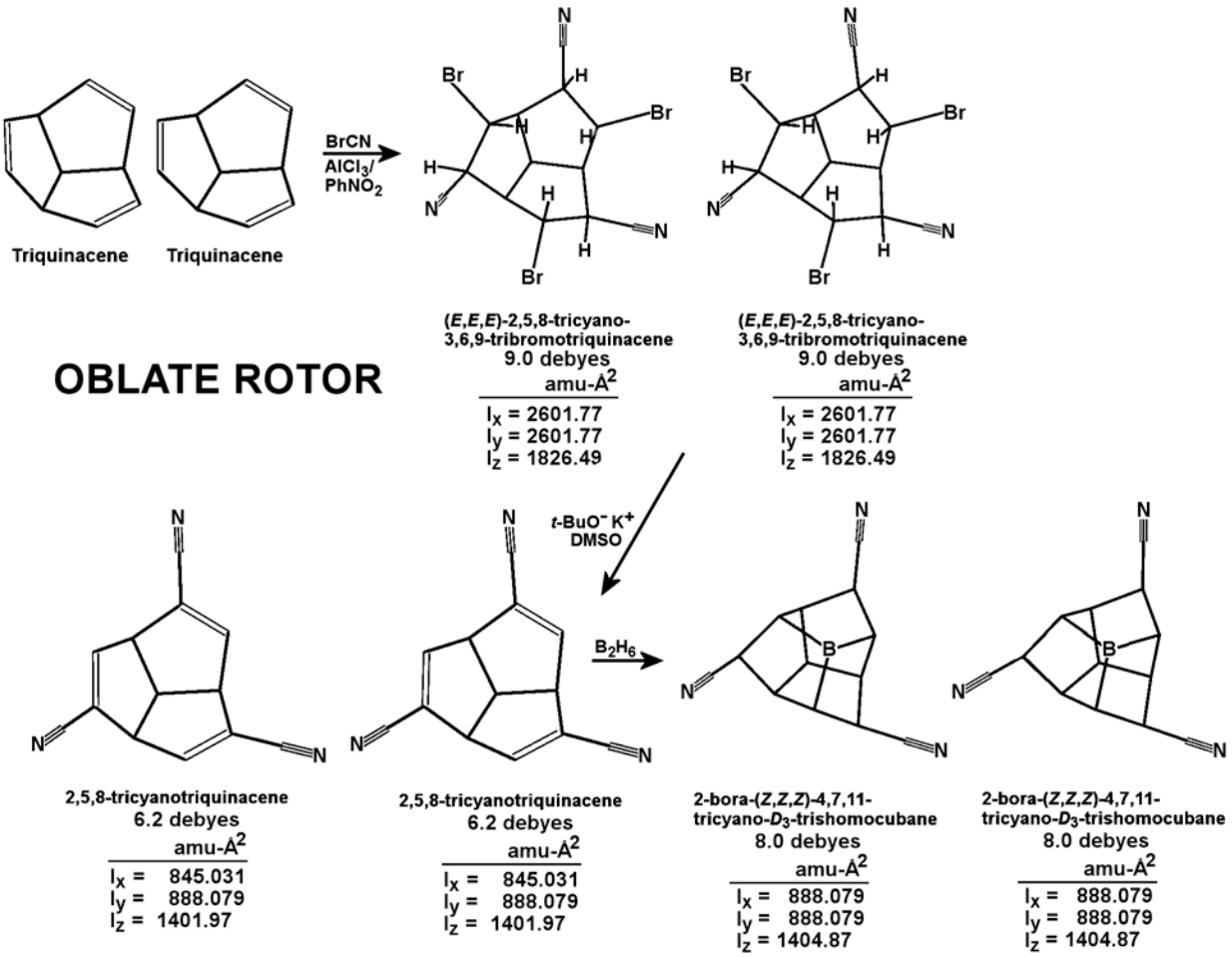
Physics is healed if enantiomers' rotational spectra are not *exactly* identical and/or not *exactly* superposed, or show 3:1 broadened lines. They are then opposite shoes differentially embedded in chiral anisotropic vacuum background (a trace left foot). Observe physical theories' naked common mode failure.

Shodden*freude*! Baryogenesis is sourced. The Tully-Fisher relation is Milgrom acceleration from Noetherian angular momentum conservation leakage in trace chiral anisotropic vacuum. General relativity is more likely Einstein-Cartan-Sciama-Kibble theory. Non-classical gravitation theories including M-theory; the standard model, and SUSY must be rederived.

If CHI proves not to be a good measure of physics' geometric chirality divergence, observe spiky molecule enantiomers: norborn-2-ene-(*E*)-5,6-dicarbonitrile (#11)**[40,41]**, norbornane-(*E*)-2,3-dicarbonitrile (#12)**[42,43,44]**, and norbornane-(*E*)-2,3-(*E*)-5,6-tetracarbonitrile (#13)**[45]**. Chiroptical measures are not coupled to mass distribution, #14 and #15**[47.47]**. More sophisticated molecule manipulation, trapping, cooling, and spectrometry would be definitive. Neutral current Z^0 exchange, large atomic number atoms' parity non-conservation, is unrelated**[48]**.



An oblate rotor with a large dipole moment is a $\boldsymbol{C}_3$-symmerty propeller. It also offers a simple and intense microwave rotational spectrum. One can imagine a provisional entry into such structures.



[1] M. R. Buckley, A. H.G. Peter, "Gravitational probes of dark matter physics," arXiv:1712.06615

[2] K. Abe, *et al*. (Super-Kamiokande Collaboration), "Search for proton decay via $p \rightarrow e^{+}\pi^{0}$ and $p \rightarrow \mu^{+}\pi^{0}$ in 0.31 megaton • years exposure of the Super-Kamiokande water Cherenkov detector," *Phys. Rev. D* **95**(1), 012004 (2017), DOI:10.1103/PhysRevD.95.012004, arXiv:1610.03597

[3] A. B. Kaliyar, "Recent measurements of branching fractions and CP asymmetries of charmless hadronic B meson decays at Belle," arXiv:1710.02962

[4] R. H. Cyburt, B. D. Fields, K. A. Olive, T-H Yeh "Big bang nucleosynthesis: Present status" *Rev. Mod. Phys.* **88**(1), 015004 (2016), DOI:10.1103/RevModPhys.88.015004, arXiv:1505.01076

[5] K. Pasmatsiou, C. G. Tsagas, J. D. Barrow, "Kinematics of Einstein-Cartan universes," *Phys. Rev. D* **95**(10), 104007 (2017), DOI:10.1103/PhysRevD.95.104007, arXiv:1609.09275

[6] N. J. Popławski, "Cosmology with torsion: An alternative to cosmic inflation," *Phys. Lett. B*, **694**(3) 181 (2010), DOI:10.1016/j.physletb.2010.09.056, arXiv:1007.0587

[7] G. Dvali, "Topological Origin of Chiral Symmetry Breaking in QCD and in Gravity," arXiv:1705.06317

[8] E. Witten, "Symmetry and Emergence," arXiv:1710.01791

[9] B. Famaey, and S. S. McGaugh, "Modified Newtonian Dynamics (MOND): Observational Phenomenology and Relativistic Extensions," *Living Rev. Relativ.* **15**(10) (2012), DOI:10.12942/lrr-2012-10, arXiv:1112.3960

[10] A. N. Ivanov, M. Wellenzohn, "Einstein-Cartan Gravity with Torsion Field Serving as Origin for Cosmological Constant or Dark Energy Density," *Astrophys. J.*, **829**(1) 47 (2016), DOI:10.3847/0004-637X/829/1/47, arXiv:1607.01128

[11] A. Golovnev, T. Koivisto, M/ Sandstad, "On the covariance of teleparallel gravity theories," *Class. Quantum Grav.* **34**(24) 145013 (2017), DOI10.1088/1361-6382/aa7830, arXiv:1701.06271

[12] M. Petitjean, "Chirality in metric spaces," *Optim. Lett.* (2017), DOI:10.1007/s11590-017-1189-7

[13] M. Petitjean "Chiral mixtures" *J. Math. Phys.* **43**(8) 4147 (2002), DOI:10.1063/1.1484559

[14] M. Petitjean "On the root mean square quantitative chirality and quantitative symmetry measures" *J. Math. Phys.* **40**(9), 4587 (1999), DOI:10.1063/1.532988
[15] D. I. Sharapa, I. A. Levandovskiy, T. E. Shubina "Axial D_3-trishomocubane derivatives with potential: dreams or reality?" *Curr. Org. Chem.* **16**(22), 2623 (2012) DOI:10.2174/138527212804004508
[**16**] M. A. Brimble, L. J. Duncalf, D. C. W. Reid, T. R. Roberts, "Addition of cyclopentadiene and 2-trimethylsilyloxyfuran to quinones bearing a menthyl ester chiral auxiliary," *Tetrahedron* **54**(20) 5363 (1998), DOI:10.1016/S0040-4020(98)00211-7
[17] H. Bonnard, L. Ferruccio, P. Gauthier, J-Senet, "Process for the synthesis of aliphatic, cycloaliphatic or araliphatic chloroformates," US Pat. 6696590 (2004)
[18] A. Bavley,W. C. Bailey, Jr,, "Smoking tobacco composition," US Pat. 331222 (1967)
[19] A. A. Waghmare, R. M. Hindupur, H. N. Pati, "Propylphosphonic anhydride (T3P®): An expedient reagent for organic synthesis," *Rev. J. Chem.* **4**(2) 53 (2014), DOI:10.1134/S2079978014020034
[20] http://www.euticals.com/attachments/article/11/EUTICALS_T3P-Coupling-Agents_2012_final_web.pdf
[21] G. A. Boswell Jr. W. C. Ripka R. M. Scribner C. W. Tullock, "Fluorination by sulfur tetrafluoride," *Organic Reactions*, **21** 2 (1974), DOI:10.1002/0471264180.or021.01
[22] C-l Wang, "Fluorination by sulfur tetrafluoride." *Organic Reactions*, **34** 319 (1985), DOI:10.1002/0471264180.or034.02
[23] C-l Wang, "Reagents for Organic Synthesis," Sulfur tetrafluoride, DOI:10.1002/047084289X.rs137
[**24**] L. A. Paquette, J. H. Barrett, "2,7-Dimethyloxepin," *Org. Synth.* **49**, 62 (1969), *Org. Synth. Coll. Vol.* **5**, 467 (1973), DOI:10.15227/orgsyn.049.0062
[**25**] E. Vogel, H. Günther, "Benzene Oxide-Oxepin Valence Tautomerism," *Angew Chem. Int. Ed.*, **6**(5) 385 (1967), DOI:10.1002/anie.196703851
[**26**] S. Cossu, S. Battaggia, O. De Lucchi, "Barrelene, a New Convenient Synthesis," *J. Org. Chem.* **62**(12) 4162 (1997), DOI:10.1021/jo962267f
[**27**] T. Preuß, D. S. Yufit, J. A. K. Howa, et al.,"4,7,11-Triheterotrishomocubanes– Propeller Shaped Highly Symmetrical Chiral Molecules Derived from Barrelene." *Eur. J. Org. Chem.* **2006**(11), 2590 (2006), DOI:10.1002/ejoc.200600019
[28] K. Takai, T. Kakiuchi, K. Utimoto, "A Dramatic Effect of a Catalytic Amount of Lead on the Simmons-Smith Reaction and Formation of Alkylzinc Compounds from Iodoalkanes. Reactivity of Zinc Metal: Activation and Deactivation," *J. Org. Chem.*, **59**(10), 2671 (1994), DOI:10.1021/jo00089a003
[29] T. Fukuyama, L. Li, A. A. Laird, R. K. Frank. "Stereocontrolled total synthesis of (±)-cyanocycline A, " *J. Am. Chem. Soc.*, **109**(5), 1587 (1987), DOI:10.1021/ja00239a059
[30] M. Mascal, N. Hafezi, N. K. Meher, J. C. Fettinger, "Oxatriquinane and Oxatriquinacene: Extraordinary Oxonium Ions." *J. Am. Chem. Soc.*, **130**(41), 13532 (2008). DOI: 10.1021/ja805686u
[31] A. K. Gupta, G. S. Lannoye, G. Kubiak, J. Schkeryantz, S. Wehrli, J. M. Cook, "General approach to the synthesis of polyquinenes. VIII. Synthesis of triquinacene, 1,10-dimethyltriquinacene, and 1,10-cyclohexanotriquinacene." *J. Am. Chem. Soc.*, **111**(6), 2169 (1989), DOI: 10.1021/ja00188a035
[32] M. Mascal, M. Lera, A. J. Blake, "Azatriquinanes. 2.1 Synthesis of Azatriquinadiene and Azatriquinacene," *J. Org. Chem.*, **65**(21) 7253 (2000), DOI: 10.1021/jo005571o
[33] H. C. Brown, E. J. Negishi, "Perhydro-9b-boraphenalene and perhydro-9b-phenalenol," *Org. Synth.*, **61**, 103 (1983), DOI:10.15227/orgsyn.061.0103
[34] D. W. Stephan, "The broadening reach of frustrated Lewis pair chemistry," *Science*, **354**(6317) aaf7229 (2016), DOI:10.1126/science.aaf7229
[35] S. R. Domingos, C. Pérez, C. Medcraft, P. Pinachoad, M. Schnell, "Flexibility unleashed in acyclic monoterpenes: conformational space of citronellal revealed by broadband rotational spectroscopy," *Phys. Chem. Chem. Phys.*, **18**(25), 16682 (2016), DOI:10.1039/C6CP02876D
[36] C. Medcraft, M. Schnell, "A Comparative Study of Two Bicyclic Ethers, Eucalyptol and 1,4-Cineole, by Broadband Rotational Spectroscopy," *Z. Phys. Chem.* **230**(1) 1 (2016), DOI: https://doi.org/10.1515/zpch-2015-0643
[37] C. Medcraft, R. Wolf, M. Schnell, "High-Resolution Spectroscopy of the Chiral Metal Complex [CpRe(CH3)(CO)(NO)]: A Potential Candidate for Probing Parity Violation," *Angew. Chem. Int. Ed.* **53**(43) 11656 (2014), DOI:10.1002/anie.201406071
[38] E. Fliege, H. Dreizler, A. P. Cox, "Nitrogen-14 Nuclear Quadrupole Coupling and Centrifugal Distortion of Pivalonitrile," *Z. Naturforsch.* **41**(11), 1307 (1986), DOI:10.1515/zna-1986-1107

[39] R. Dwiliński, M. Palczewska, P. Kaczor, K. Korona, et al., "Collisional Broadening of the J = 7 ⇐ 6 Transition Of t-Butyl Cyanide By CH3CN, OCS, CO2 and Helium," *Acta Physica Polonica A*, **81**(6) 613 (1992). DOI:10.12693/APhysPolA.82.613

[40] G. O. Jones, V. A. Guner‡, and K. N. Houk, "Diels−Alder Reactions of Cyclopentadiene and 9,10-Dimethylanthracene with Cyanoalkenes: The Performance of Density Functional Theory and Hartree−Fock Calculations for the Prediction of Substituent Effects," *J. Phys. Chem. A*, **110**(4), 1216 (2006), DOI:10.1021/jp052055z

[41] Arbuzov, B.A. & Vereshchagin, A.N., "Dipole moments of adducts of fumaronitrile and maleonitrile with cyclic dienes," *Russ. Chem. Bull.* **15**, 1674 (1966). DOI:10.1007/BF00848701

[42] C. E. Miller, "Hydrogenation with diimide," *J. Chem. Educ.*, **42**(5), 254 (1965), DOI:10.1021/ed042p254

[43] Pasto, D. J. and Taylor, R. T. "Reduction with Diimide," *Organic Reactions*, **40**(2), 91 (2004), DOI: 10.1002/0471264180.or040.02

[44] J. Thiele, "Ueber Azodicarbonsäure (Diimiddicarbonsäure)." *Ann.*, **271,** 127 (1892) DOI:10.1002/jlac.18922710120

[45] Frank M Cowen James K Dixon, US Pat. 2653963 (1951)

[46] T. D. Crawford, M. C. Tam, M. L. Abrams "The Current State of *Ab Initio* Calculations of Optical Rotation and Electronic Circular Dichroism Spectra," *J. Phys. Chem A*, **111**(48) 12057 (2007), DOI: 10.1021/jp075046u

[47] K. B. Wiberg, Y-g. Wang, S. M. Wilson, P. H. Vaccaro, J. R. Cheeseman, "Sum-over-States Calculation of the Specific Rotations of Some Substituted Oxiranes, Chloropropionitrile, Ethane, and Norbornenone," *J. Phys. Chem A*, **110**(51) 13995 (2006), DOI: 10.1021/jp0655221

[48] B. M. Roberts, V. A. Dzuba, V. V. Flambaum, "Parity and Time-Reversal Violation in Atomic Systems," *Annu. Rev. Nucl. Part. Sci*., **65**(63-86), 63 (2015), DOI:10.1146/annurev-nucl-102014-022331, arXiv:1412.6644