Supplementary Information

Deciphering the Origin of the ^{13}C NMR Anomaly in Cyclic Ketones

Binod Kumar Oram[a,b], Saiprakash Rout[a,b], Akshay Kumar Sahu[a,b], and Himansu S. Biswal[a,b]*

a. School of chemical sciences
National Institute of Science Education and Research (NISER)
PO- Bhimpur-Padanpur, Via-Jatni, District- Khurda, PIN - 752050, Bhubaneswar, India
E-mail: himansu@niser.ac.in, Phone no. +91-674-2494 185/186

b. Homi Bhabha National Institute
Training School Complex, Anushakti Nagar, Mumbai 400094, India

Table of Contents

1. Supplementary Figures

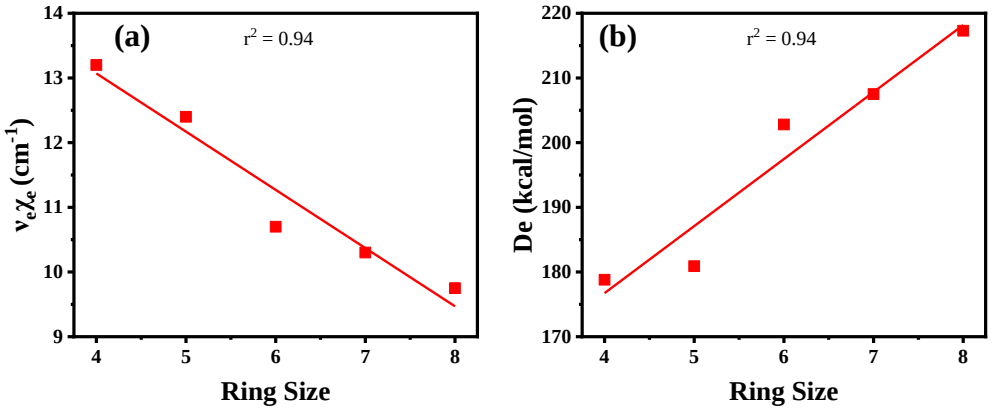

Figure S1. The correlation plot showing the variation of a) anharmonicity constant ($\nu_e\chi_e$) observed for carbonyl stretching frequency mode, b) spectroscopic dissociation energy (De) of C=O bond with change in ring size. The anharmonicity constant, dissociation energy shows a very good linear correlation.

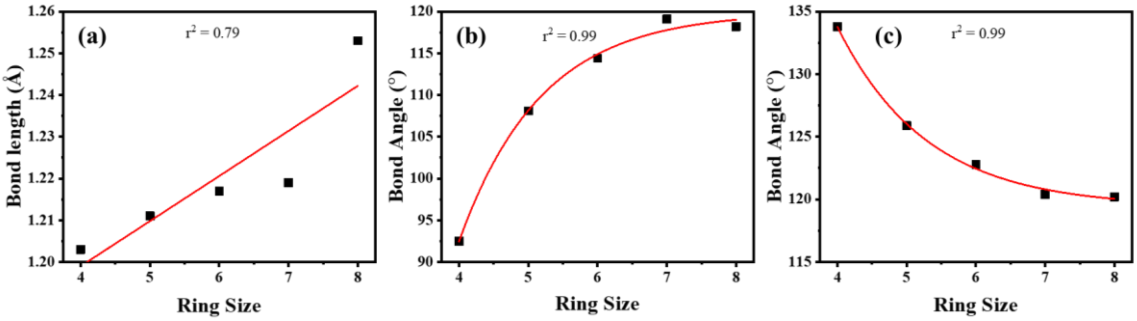

Figure S2. The correlation plot showing the variation of a) C=O Bond Length, b) ∠CCC angle, and c) ∠CCO angle with change in ring size. The C=O bond length shows a poor linear correlation with ring size, whereas the bond angles were found to show very good exponential correlation with ring size.

4. Supplementary Tables

Table S1. Fundamental ($\nu_{1\leftarrow0}$), first ($\nu_{2\leftarrow0}$) and second overtone ($\nu_{3\leftarrow0}$), anharmonicity constant ($\nu_e\chi_e$), dissociation energy (D_e), and force constant (K) of the carbonyl bond of the cyclic ketones. Also, change in geometrical parameters of the cyclic ketones with change in ring size is given.

Ketones	$\boldsymbol{\nu_{1\leftarrow0}}$ **(cm^{-1})**	$\boldsymbol{\nu_{2\leftarrow0}}$ **(cm^{-1})**	$\boldsymbol{\nu_{3\leftarrow0}}$ **(cm^{-1})**	$\boldsymbol{\nu_e\chi_e}$ **(cm^{-1})**	**C=O bond length (Å)**	**<C-C-C angle (°)**	**<C-C=O angle (°)**
4-CK	1788.5	3557.0	5286.5	13.2	1.203	92.5	133.8
5-CK	1748.9	3467.0	5172.1	11.9	1.211	108.1	125.9
6-CK	1717.1	3414.6	5087.4	10.7	1.217	114.4	122.8
7-CK	1704.6	3386.2	5052.3	10.3	1.219	119.1	120.4
8-CK	1702.2	3385.5	5048.1	9.8	1.253	118.2	120.2

Table S2. Principal components of the carbonyl ^{13}C chemical shift tensor and the PAC on C and O atom.

Ketones	**Calculated**				**PAC on 'C'**	**PAC on 'O'**
	$\boldsymbol{\delta_{11}}$	$\boldsymbol{\delta_{22}}$	$\boldsymbol{\delta_{33}}$	$\boldsymbol{\delta_{Total}}$		
4-CK	282.8	246.3	94.8	**208.0**	0.179	-0.297
5-CK	278.6	246.5	125.1	**216.7**	0.198	-0.325
6-CK	281.5	261.4	82.7	**208.5**	0.193	-0.326
7-CK	284.6	256.4	93.0	**211.3**	0.069	-0.281
8-CK	284.8	266.6	89.8	**213.7**	0.200	-0.329

Table S3. Calculated principal components of the chemical shielding tensors and their corresponding diamagnetic and paramagnetic components of the five cyclic ketones.

	4-CK	**5-CK**	**6-CK**	**7-CK**	**8-CK**
$\boldsymbol{\sigma_{11}}$	-100.1	-95.7	-98.9	-100.5	-86.1
$\boldsymbol{\sigma_{11}}$**-dia**	251.2	257.1	262.7	267.7	261.2
$\boldsymbol{\sigma_{11}}$**-para**	-351.3	-352.7	-361.6	-368.3	-347.3
$\boldsymbol{\sigma_{22}}$	-60.1	-64.0	-67.8	-58.3	-52.1
$\boldsymbol{\sigma_{22}}$**-dia**	267.4	265.1	269.9	250.1	251.0
$\boldsymbol{\sigma_{22}}$**-para**	-327.5	-329.2	-337.7	-308.4	-303.0
$\boldsymbol{\sigma_{33}}$	86.3	57.0	89.0	72.0	44.6
$\boldsymbol{\sigma_{33}}$**-dia**	219.3	222.6	239.5	220.2	231.9
$\boldsymbol{\sigma_{33}}$**-para**	-133.0	-165.5	-150.5	-148.2	-187.3
$\boldsymbol{\sigma_{iso}}$	-24.7	-34.2	-25.9	-28.9	-31.2

Table S4. The orbital contributions towards chemical shielding tensors of carbonyl carbon, obtained from NCS analysis for all the studied cyclic ketones.

4-CK	**O (LP)**	**O (LP)**	**C2-C3**	**C3-C4**	**C3-O9**	**C3-O9**	$\Sigma\sigma_{ii}$
σ_{11}	-41.1	-2.7	-37.6	-37.6	-160.7	11.5	-268.2
σ_{22}	2.5	-70.8	-209.9	-209.5	12.8	37.1	-437.8
σ_{33}	-8.6	-4.4	-32.3	-33.3	-50.2	6.9	-121.9
5-CK	**O (LP)**	**O (LP)**	**C2-C3**	**C3-C4**	**C3-O9**	**C3-O9**	
σ_{11}	-40.4	-2.8	-33.8	-33.8	-162.6	7.2	-266.2
σ_{22}	2.5	-69.0	-214.0	-213.5	12.7	50.8	-430.5
σ_{33}	-7.1	-7.1	-49.1	-49.0	-33.9	6.9	-139.3
6-CK	**O (LP)**	**O (LP)**	**C1-C2**	**C1-C6**	**C1-O7**	**C1-O7**	
σ_{11}	-40.4	-1.3	-31.3	-31.2	-157.5	-5.0	-266.7
σ_{22}	2.5	-67.0	-210.2	-210.4	12.6	37.4	-435.1
σ_{33}	-3.9	-4.0	-45.3	-45.1	-25.4	7.0	-116.7
7-CK	**O (LP)**	**O (LP)**	**C4-C6**	**C6-C7**	**C6-O18**	**C6-O18**	
σ_{11}	-36.6	-7.2	-102.0	13.9	-141.8	-13.4	-287.1
σ_{22}	-0.3	-59.4	-150.4	-262.7	1.2	53.2	-418.4
σ_{33}	-5.9	-1.6	-54.5	-49.4	-3.1	7.1	-107.4
8-CK	**O (LP)**	**O (LP)**	**C1-C2**	**C1-C17**	**C1-O23**	**C1-O23**	
σ_{11}	-39.5	-3.3	-63.5	-6.0	-160.2	-6.6	-279.1
σ_{22}	1.9	-62.9	-195.5	-251.7	9.7	46.9	-451.6
σ_{33}	-6.1	-2.3	-52.8	-48.5	-12.1	7.3	-114.5

Table S5. Root mean square deviation (RMSD) of the nuclear frameworks quantifying the structural relaxation upon the n → π* electronic transition.

Ketone	**4-CK**	**5-CK**	**6-CK**	**7-CK**	**8-CK**
RMSD value	0.3434	0.2493	0.4627	0.4349	0.9991

Table S6. Cartesian coordinates (in Å), frequencies (in cm^{-1}) and energetics (in Hartree) of the optimized geometries at B97D/aug-cc-pVTZ level of theory.

	Co-ordinates				**Frequencies**		
4-CK ($\mathbf{E_{HF}}$: **−231.1579515**)	C	-0.091645000	-1.478115000	0.000000000	23.7	382.0	439.9
	C	-0.091645000	-0.378529000	1.111968000	591.6	648.1	704.1
	C	0.057483000	0.678448000	0.000000000	807.0	877.2	906.1
	C	-0.091645000	-0.378529000	-1.111968000	924.7	1031.9	1061.5
	H	-0.964465000	-2.135289000	0.000000000	1142.6	1185.6	1189.4
	H	0.815051000	-2.088390000	0.000000000	1197.5	1230.1	1380.3
	H	0.725755000	-0.398667000	1.842057000	1398.2	1451.7	1793.0
	H	-1.039420000	-0.278085000	1.655836000	2970.6	2975.7	3005.4
	O	0.260182000	1.864691000	0.000000000	3028.4	3033.9	3066.7
	H	0.725755000	-0.398667000	-1.842057000			
	H	-1.039420000	-0.278085000	-1.655836000			
5-CK ($\mathbf{E_{HF}}$: **−270.4847991**)	C	1.379925130	0.737511110	-0.236173350	95.9	225.8	431.0
	C	-0.030119000	1.237580840	0.121880160	454.8	545.1	565.3
	C	-0.931719520	0.000015090	-0.000220850	675.3	777.4	811.1
	C	-0.030098930	-1.237542260	-0.122164380	856.9	889.3	925.9
	C	1.379822280	-0.737513650	0.236427540	928.1	985.2	1098.5
	H	2.177759480	1.327914100	0.225210400	1126.6	1130.6	1184.4
	H	-0.411124380	2.060992360	-0.490190150	1214.6	1256.1	1265.8
	H	-0.075007690	1.561646520	1.172494200	1299.0	1302.9	1403.7
	O	-2.143172800	0.000016200	-0.000272490	1405.4	1453.2	1462.9
	H	-0.074595830	-1.561426740	-1.172854700	1749.4	2951.6	2952.2
	H	2.177817590	-1.327935620	-0.224653430	2959.7	2965.4	3021.3
	H	1.521118650	-0.774165430	1.324629980	3027.1	3034.6	3035.9
	H	1.521641650	0.774154470	-1.324320870			
	H	-0.411320640	-2.061051980	0.489634940			
6-CK ($\mathbf{E_{HF}}$: **−309.7895126**)	C	-1.160425000	0.000000000	0.077084000	87.5	174.7	294.0
	C	-0.390454000	-1.282407000	0.375413000	397.7	407.4	462.4
	C	1.006275000	-1.265145000	-0.290970000	485.2	639.5	723.4
	C	1.790115000	0.000002000	0.088505000	736.3	807.1	846.5
	C	1.006273000	1.265145000	-0.290973000	860.0	883.3	961.0
	C	-0.390455000	1.282406000	0.375416000	990.3	1020.2	1027.7
	O	-2.288601000	-0.000001000	-0.380586000	1081.3	1102.3	1197.6

	H	-0.987933000	-2.141227000	0.054705000	1208.3	1229.3	1249.3
	H	-0.254817000	-1.339973000	1.466672000	1288.1	1298.7	1327.5
	H	1.560456000	-2.166599000	-0.002586000	1333.7	1338.6	1420.2
	H	0.880397000	-1.298224000	-1.382242000	1428.5	1445.3	1448.2
	H	2.768350000	0.000001000	-0.408163000	1460.5	1721.8	2933.8
	H	1.976282000	0.000003000	1.172904000	2935.7	2940.7	2948.2
	H	1.560451000	2.166602000	-0.002592000	2950.2	2995.0	2999.1
	H	0.880391000	1.298221000	-1.382244000	3004.5	3032.9	3034.6
	H	-0.987935000	2.141227000	0.054711000			
	H	-0.254812000	1.339969000	1.466673000			
	C	0.548357000	-1.629086000	-0.142986000	46.2	165.1	219.8
	C	1.807109000	-0.753946000	-0.078682000	301.7	318.2	332.7
	C	1.629427000	0.708749000	-0.518067000	446.5	477.1	498.5
	C	-0.635615000	-1.126100000	0.724491000	582.7	676.3	758.8
	C	0.723676000	1.537635000	0.415011000	797.5	819.7	832.2
	C	-1.368411000	0.010782000	0.027230000	890.9	916.5	954.0
	C	-0.778449000	1.418612000	0.112267000	974.1	1002.6	1018.7
	H	0.209400000	-1.724933000	-1.183706000	1063.7	1128.1	1134.6
	H	2.185569000	-0.758664000	0.954676000	1167.9	1190.8	1227.4
7-CK	H	1.230781000	0.744190000	-1.543165000	1249.2	1264.2	1302.3
(**E_{HF}: −349.0856762**)	H	0.924624000	1.248675000	1.455969000	1324.1	1334.0	1342.8
	H	-0.251570000	-0.796694000	1.699945000	1344.4	1352.0	1402.7
	H	0.809078000	-2.639273000	0.196059000	1437.7	1440.7	1446.3
	H	2.583005000	-1.221213000	-0.699593000	1455.8	1457.1	1707.9
	H	2.622363000	1.174713000	-0.552788000	2930.3	2936.3	2940.5
	H	-1.355282000	-1.936477000	0.875100000	2948.0	2950.6	2955.8
	H	0.991265000	2.598186000	0.332790000	2984.4	2989.5	2994.1
	O	-2.390881000	-0.193391000	-0.604040000	3001.2	3010.7	3036.2
	H	-1.355637000	1.938060000	0.893120000			
	H	-1.023114000	1.920679000	-0.831672000			
	C	-1.534410000	-0.209692000	0.046832000	70.3	135.2	171.0
	C	-0.769456000	-1.331966000	-0.647987000	206.8	270.7	306.0
8-CK	C	0.904614000	1.355234000	0.642674000	343.4	410.9	443.9
(**E_{HF}: -388.3778352**)	C	0.551004000	-1.726158000	0.077526000	490.4	508.1	628.8
	C	2.085147000	0.381988000	0.457566000	673.9	716.4	759.1
	C	1.796676000	-0.912290000	-0.329855000	794.7	838.9	866.4

	H	-0.541868000	-1.066762000	-1.688337000	906.7	917.2	941.0
	H	0.391501000	-1.683405000	1.162847000	960.8	1012.9	1030.6
	H	0.240446000	0.956498000	1.419908000	1064.5	1079.9	1085.3
	H	2.461148000	0.113023000	1.454107000	1130.2	1171.5	1189.9
	H	-1.437382000	-2.200451000	-0.645715000	1218.0	1236.5	1246.4
	H	1.297064000	2.295983000	1.046756000	1279.1	1302.0	1311.5
	H	0.741042000	-2.777635000	-0.167038000	1319.2	1333.1	1348.4
	H	2.906991000	0.903027000	-0.053531000	1354.3	1365.7	1423.5
	H	2.680065000	-1.555070000	-0.223242000	1441.3	1441.6	1449.3
	H	1.724166000	-0.685500000	-1.402410000	1452.5	1480.0	1481.6
	C	-1.393293000	1.200653000	-0.511611000	1706.8	2937.6	2942.2
	H	-1.936199000	1.877871000	0.156374000	2946.4	2958.3	2961.3
	H	-1.875844000	1.229618000	-1.500385000	2961.5	2974.1	2978.9
	C	0.085010000	1.630443000	-0.646164000	2992.1	3002.7	3008.8
	H	0.535161000	1.105927000	-1.496599000	3013.4	3025.4	3030.4
	H	0.108407000	2.696142000	-0.899589000			
	O	-2.205806000	-0.442317000	1.037872000			

5. Python script for overlap integral calculation

```
import numpy as np
import sys
import os
def read_cube(filename):
    """ Reads a Gaussian Cube file. """
    if not os.path.exists(filename):
        print(f"Error: '{filename}' not found.")
        sys.exit(1)
    with open(filename, 'r') as f:
        lines = f.readlines()
    try:
        natoms = int(lines[2].split()[0])
        origin = np.array([float(x) for x in lines[2].split()[1:4]])
        nx, dx, _, _ = [float(x) for x in lines[3].split()]
        ny, _, dy, _ = [float(x) for x in lines[4].split()]
        nz, _, _, dz = [float(x) for x in lines[5].split()]
        nx, ny, nz = int(nx), int(ny), int(nz)
    except:
        print("Error parsing header.")
        sys.exit(1)
    atoms = []
    header_end = 6 + natoms
    for i in range(6, header_end):
        parts = lines[i].split()
        # Store: (Atomic Number, Coords in Bohr)
        atoms.append((int(parts[0]), np.array([float(x) for x in parts[2:5]])))
    data_str = " ".join([l.strip() for l in lines[header_end:]])
    grid = np.fromstring(data_str, sep=' ').reshape((nx, ny, nz))
    return grid, {
        'dims':(nx,ny,nz),
        'steps':(dx,dy,dz),
        'origin':origin,
        'atoms':atoms,
        'dV':abs(dx*dy*dz)
    }
def calculate_rmsd(meta_homo, meta_lumo):
    """ Calculates atomic RMSD to quantify geometric similarity. """
    coords_h = np.array([a[1] for a in meta_homo['atoms']])
    coords_l = np.array([a[1] for a in meta_lumo['atoms']])
    if coords_h.shape != coords_l.shape:
        return None
    diff = coords_h - coords_l
    rmsd = np.sqrt(np.sum(diff**2) / len(coords_h))
    print("\n" + "="*50)
    print(f" GEOMETRIC ANALYSIS (Similarity Check)")
    print("="*50)
    print(f"Atomic RMSD Shift: {rmsd:.6f} Bohr")
    if rmsd < 0.02:
        print("Status: IDEAL")
    elif rmsd < 0.15:
        print("Status: MODERATE DISTORTION")
    else:
        print("Status: HIGH DISTORTION")
```

```
    print("="*50)
    return rmsd
def list_carbon_atoms(atoms):
    print("\n--- Candidate Carbon Atoms ---")
    valid = []
    for i, (z, coords) in enumerate(atoms):
        if z == 6:
            print(f"{i+1:3d} | C | {coords}")
            valid.append(i+1)
    return valid
def calculate_isotropic_detailed(grid_homo, grid_lumo, meta, center_idx):
    """ Calculates L and L/r^3 for X, Y, Z axes. """
    nx, ny, nz = meta['dims']
    dx, dy, dz = meta['steps']
    ox, oy, oz = meta['origin']
    # Center Coordinates
    atom_z, center_coords = meta['atoms'][center_idx - 1]
    print(f"\nCentering on Atom {center_idx} (Z={atom_z}) at {center_coords}")
    # Generate Relative Grids
    x_c = np.linspace(ox, ox + (nx-1)*dx, nx) - center_coords[0]
    y_c = np.linspace(oy, oy + (ny-1)*dy, ny) - center_coords[1]
    z_c = np.linspace(oz, oz + (nz-1)*dz, nz) - center_coords[2]
    X, Y, Z = np.meshgrid(x_c, y_c, z_c, indexing='ij')
    # Radial Terms
    R_sq = X**2 + Y**2 + Z**2 + 1e-6
    R_cubed = R_sq**1.5
    # Gradients of HOMO
    grad = np.gradient(grid_homo, dx, dy, dz)
    d_dx, d_dy, d_dz = grad[0], grad[1], grad[2]
    # Define Operators (L = -i * (r x grad))
    Lx_op = -1j * (Y * d_dz - Z * d_dy)
    Ly_op = -1j * (Z * d_dx - X * d_dz)
    Lz_op = -1j * (X * d_dy - Y * d_dx)
    operators = {'X': Lx_op, 'Y': Ly_op, 'Z': Lz_op}
    total_numerator = 0.0
    print("\n" + "="*85)
    print(f"{'Axis':^5} | {'Mixing <L>':^22} | {'Paramagnetic <L/r3>':^22} | {'Product (Real)':^18}")
    print("="*85)
    for axis, op in operators.items():
        integrand_L = grid_lumo * op
        val_L = np.sum(integrand_L) * meta['dV']
        integrand_Lr3 = integrand_L / R_cubed
        val_Lr3 = np.sum(integrand_Lr3) * meta['dV']
        # Physical contribution is the real part of the product
        product = (val_L * val_Lr3).real
        total_numerator += product
        print(f"{axis:^5} | {abs(val_L):^22.4e} | {abs(val_Lr3):^22.4e} | {product:^18.4e}")
    print("-" * 85)
    print(f"{'TOTAL':^5} | {'---':^22} | {'---':^22} | {total_numerator:^18.4e}")
    print("="*85)
    return total_numerator
# --- MAIN ---
if __name__ == "__main__":
    print("-" * 60)
    print(" NMR PARAMAGNETIC NUMERATOR CALCULATOR (with RMSD)")
```

```
    print("-" * 60)
    f_homo = input("\nHOMO cube (Ground State Geometry: MOvalue-n.cub):\n> ").strip().replace("","")
    f_lumo = input("\nLUMO cube (Excited State Geometry: MOvalue-pi.cub):\n> ").strip().replace("","")
    g_homo, m_homo = read_cube(f_homo)
    g_lumo, m_lumo = read_cube(f_lumo)
    # 1. Quantify Structural Similarity
    rmsd_val = calculate_rmsd(m_homo, m_lumo)
    # 2. Fix Grid Mismatch (The Resizer Hack)
    if g_homo.shape != g_lumo.shape:
        print(f"\n[!] Grid mismatch detected: HOMO {g_homo.shape} vs LUMO {g_lumo.shape}")
        min_shape = tuple(min(s1, s2) for s1, s2 in zip(g_homo.shape, g_lumo.shape))
        print(f"    Resizing both grids to {min_shape} for compatibility...")
        g_homo = g_homo[:min_shape[0], :min_shape[1], :min_shape[2]]
        g_lumo = g_lumo[:min_shape[0], :min_shape[1], :min_shape[2]]
        m_homo['dims'] = min_shape  # Ensure meshgrid aligns with resized data
    # 3. Choose center and calculate
    valid_list = list_carbon_atoms(m_homo['atoms'])
    try:
        c_idx = int(input("\nSelect Carbon Atom Index for Centering: ").strip())
    except ValueError:
        print("Invalid number.")
        sys.exit(1)
    total_val = calculate_isotropic_detailed(g_homo, g_lumo, m_homo, c_idx)
    print(f"\nFinal Isotropic Numerator Sum: {total_val:.6e}")
    print("Note: If RMSD is high (> 0.1), use these results with caution.")
input("\nPress Enter to exit.")"
```